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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

CARBON COMBUSTIONS IN A PLATINUM CRUCIBLE

By R. W. SHIMER.

Received February 14, 1899.

THE determination of carbon by combustion in oxygen necessitates the use of a costly and bulky combustion furnace, a porcelain or platinum tube, and a supply of pure oxygen. The gas consumption is large and the heat generated is ridiculously out of proportion to the small amount of carbon to be burned. Even with this wasteful use of gas, the temperature attained, under the conditions of gas pressure existing in some laboratories, is not always high enough to ensure the complete combustion of graphite in pig iron.

In the apparatus devised by the writer, it is proposed to use a platinum crucible, with a water-cooled stopper, in place of the porcelain or platinum tube; an ordinary small blast-lamp and Bunsen burner in place of the combustion furnace; and air instead of oxygen.

The crucible is a platinum fusion crucible of the usual shape, about $1\frac{7}{8}$ inches in diameter and $1\frac{3}{8}$ inches high. In order to stiffen the top of the crucible, a ring made of ordinary sheet copper about $\frac{3}{8}$ inch wide, brazed at the ends, is fitted closely around the extreme top of the crucible. This ring is made of sheet metal so as to give the crucible the necessary support against stretching, without, at the same time, making it too rigid.

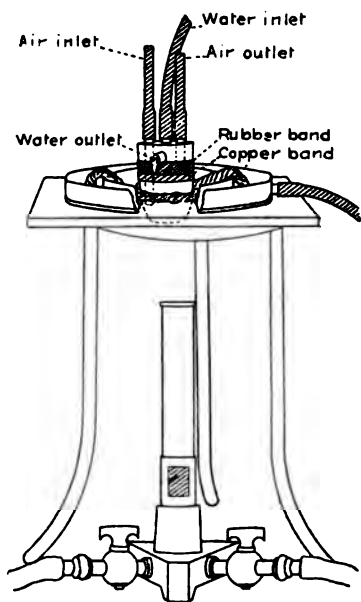


Fig. 1.

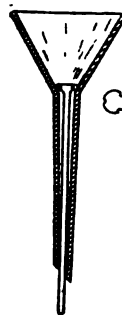


Fig. 2.

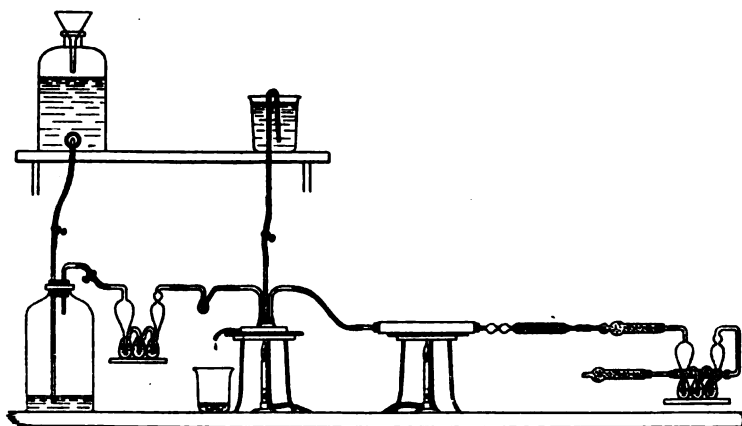


Fig. 3.

The essential part of the apparatus is the water-cooled stopper for closing the crucible. The construction of this stopper will be readily understood from the sketch. The stopper is made of sheet copper, the joints being brazed. It is, of course, essential that it should be as near perfectly circular as possible, with no indentations or imperfections in the brazing. The sides of the stopper should not flare more than the sides of the crucible at the top. Too much flare has a tendency to cause the stopper to be forced out of the crucible when under pressure.

The stopper is made somewhat smaller than the crucible opening, in order to allow space for a rubber band. This band is of pure black rubber such as can readily be obtained at most stationers. It is one-fourth to one-half inch wide and of such a length that it will stretch tightly around the lower part of the stopper. With a very little experience in putting the rubber-banded stopper into the crucible, it may be made perfectly tight with a greater degree of certainty than can the common rubber stoppers used in a porcelain combustion tube.

When the lower part of the crucible comes to a bright red heat in the course of a combustion, there is no risk whatever of burning or softening the rubber, for the band is cooled by the water passing through the stopper and by wet wick wrapped twice or more around the upper part of the crucible, the ends of the wick drawing their water from a circular copper trough kept full by the overflow from the stopper. In order to avoid any risk of softening the lower edge of the band by the heat radiating from the bottom of the crucible, the latter is always one-third to one-half full of ignited asbestos. I have used a single rubber band for as many as twenty combustions, and then discarded it only because it was becoming hard, making it more difficult to make the crucible tight.

In the train for the combustion of carbon in iron and steel, shown in the illustration, we have the following parts, beginning at the left:

1. Two aspirator bottles, the upper filled with distilled water and the tube leading to the lower bottle extending to the bottom of the latter.
2. Potassium hydroxide bulbs containing potassium hydroxide of 1.27 specific gravity.

3. A little guard bottle to retain any drops of potassium hydroxide that may be forced over from the Geissler bulbs.

4. The combustion crucible connected with its reservoir of *distilled* water for supplying the stopper; the circular trough to catch the overflow and serve as a source of water for the wet wick; the piece of stout asbestos board perforated to support the crucible at a point about half way through. Under the crucible we have the blast-lamp.

5. Next to the crucible is the cupric oxide tube, a short brass or porcelain tube, ten to twelve inches long, of small diameter. In some recent experiments, a small brass tube three-eighths inch in diameter and ten inches long, filled in its middle portion with cupric oxide, was tried in place of the porcelain tube and was found to be quite satisfactory. The brass tube is filed down at the ends and the rubber tubing is stretched over them. Although a porcelain tube is shown in the sketch, I am now using a brass tube altogether. The cupric oxide tube is supported across the top of a tripod, with a single good Bunsen burner below, to heat to a red heat one and one-half to two inches of the cupric oxide. A piece of stout asbestos board is laid across the top of the tripod to retain the heat.

6. Next to the cupric oxide tube is a glass tube filled with glass beads, wet with water and kept quite cold externally by wet wick, to retain chlorine and hydrochloric acid. The wick is wrapped about the tube, the free ends hanging in a beaker of distilled water, not shown in sketch.

7. A large calcium chloride tube.

8. The potassium hydroxide bulbs with calcium chloride tube attached.

9. A guard tube of calcium chloride.

In the preliminary experiments some trouble was experienced in getting satisfactory constant weights on the potassium hydroxide bulbs. There was a constant increase in weight. After excluding all the sources of error that at first suggested themselves, there still remained an increase in weight of from 0.0007 to 0.0018 gram. In these early experiments air was *drawn* through the apparatus. It now occurred to me that possibly the permeability of platinum at a red heat was the cause of the trouble. Air was then forced through the apparatus, with the

result that the constant weights very rarely differed more than 0.0005 gram.

It might be supposed, if platinum is permeable at a red heat, that there would be loss of carbon when pressure is used. When, however, we compare the comparatively small amount of carbon drawn into the crucible when immersed in the flame, with the large total amount of carbon burned in the flame, and then imagine a like proportion of the small weight of carbon in the crucible lost by permeation, we may conclude that the loss is inappreciable. At all events the carbon results obtained in this way agree closely with standard results obtained by combustion in a porcelain tube in oxygen. Besides, if permeability of platinum is a serious matter in carbon determinations, it is strange that the users of platinum combustion tubes have not discovered it.

In the course of these constant weight experiments, it may be interesting to note in passing, the now well-known difficulty of getting closely agreeing constant weights in stormy weather was again noticed. Another source of error in getting constant weights was noted when, on one occasion, the hydrant water used in the aspirator bottles had become somewhat stagnant. There were enough gaseous products of decomposition, or of animalcular life processes, to cause increase in weight of the potassium hydroxide bulbs, which ceased as soon as distilled water was used in the aspirator bottles. These gases passed through the first potassium hydroxide bulbs and were burned to carbon dioxide in the crucible and cupric oxide tube and were then, of course, absorbed by the weighed potassium hydroxide bulbs.

The method of solution of steel for carbon determination is the standard one by use of acidified solution of double chloride of copper and potassium. The carbon is filtered upon asbestos in the following manner: A glass rod about one inch longer than the stem of the funnel (an ordinary funnel, two and one-half inches in diameter) and small enough in diameter to pass easily through the stem, is flattened out at one end and notched at two or three places by pressing the red hot glass against the sharp corner of a file. The sketch shows the flattened and notched end of the rod; also the rod in position in the stem of the funnel.

In preparing the filter, very short fibered ignited asbestos is used, with fibers not longer than one-sixteenth inch. This is well stirred up with distilled water so as to have it well in suspension in a rather large bulk of water. A small piece of dry asbestos about the size of a pea is placed in the bottom of the funnel upon the end of the glass rod. This is to prevent the finely divided and suspended asbestos from packing into the passage, thus impeding filtration. The suction is now turned on and a little of the suspended asbestos is poured on. When this has been deposited as a fine horizontal felt, pour on more asbestos. If the asbestos fibers are short enough, a perfectly tight filter may be made with not more than one-fourth inch of asbestos. A small bulk of filter greatly facilitates subsequent transference and combustion. When dry, the carbon may usually be picked off in a thin shell by means of a pair of forceps. It is easily transferred to the empty crucible, *with the carbon side down*. It is well to have a circular piece of thin platinum foil in the bottom of the crucible. The small amount of carbon remaining in the funnel is removed by use of a little ignited asbestos. It is necessary to be careful to keep all the carbon within about one-fourth inch from the bottom of the crucible, which is not at all difficult to do. If a part of the carbon were to be one-half to three-fourths inch from the bottom, it might escape complete combustion. Graphitic carbon from pig iron is easily burned in air at the white heat attainable by the blast-lamp. After the carbon is all transferred, a little ignited asbestos is filled in on top of it.

Another way is to add a little finely divided, ignited asbestos to the solution, and to filter the carbon on a Gooch crucible. The Gooch, without its cap, is then placed on the bottom of the combustion crucible. This method has the advantage of rapid filtration, quick transference, and avoidance of contact of the carbon and traces of copper oxide with the bottom of the combustion crucible. A Gooch crucible may be made out of an old ignition crucible.

There is no reason why oxygen should not be used successfully, but, when air does the work effectually, it seems unnecessary to use oxygen. An advantage of air is that the bulbs are weighed filled with air before and after the combustion, and

there is no need to replace oxygen with air as in the oxygen method.

When getting constant weight, proceed as follows: Fill the crucible one-third full of ignited asbestos and close it, first wetting the rubber band. Saturate the wick with alcohol; it is difficult to wet it with water. Wrap a long piece of the wick twice or more *closely* around the crucible as it rests in its place in the asbestos board, and allow the ends of the wick to lie in the copper trough as shown in the sketch. When a brass cupric oxide tube is used, a little wet wick wrapped several times about each end inside of the rubber connections and hanging in beakers of water, will avoid all risk of burning. The moisture tube is disconnected and filled with cold distilled water and the excess is allowed to drain out by holding the tube in a vertical position. It is then connected as shown in the sketch. Open the clamp and allow water to run out of the stopper. Now put the Bunsen flame under the crucible and the middle of the cupric oxide tube, covering the latter with a piece of asbestos board. Open the Hofmann clamp between the upper and lower aspirator bottles and leave it fully open. Open the Hofmann clamp between the lower aspirator bottle and the potassium hydroxide bulb and regulate the passage of air by this clamp alone. Let air bubble through the apparatus, rather more rapidly than in oxygen combustion, for twenty minutes. Detach and weigh with the usual precautions. A second weight nearly always agrees well with the first. My constant weights with this apparatus have been steadily better than I have ever been able to get with the combustion furnace and oxygen, which may be attributed both to the use of air all through and to the absence of the disturbing influence of the hot furnace near the bulbs to be weighed, and the moisture-laden air resulting from the burning of large volumes of gas. When the constant weight is obtained, the carbon is transferred to the crucible as described and the combustion is begun, after, of course, testing the apparatus for tightness. Before putting the stopper into the crucible it is best to wet the rubber band with the wet finger. This prevents friction and ensures a tight crucible. In putting in the stopper do not brace the thumb against the overflow tube, for there is great risk of bending the stopper at the base of the over-

flow. Be sure that water is running from the stopper and that the cupric oxide tube is red hot for from one and one-half to two inches, then turn on the air at the speed of about three bubbles per second and bring a small blast-lamp flame immediately under the crucible so as to heat the bottom to a bright red heat, extending at least one-fourth inch from the bottom. A large flame is to be avoided. The bottom of the crucible should be flat or, better, slightly convex—*never concave*. Combustion begins immediately, and in one or two minutes carbon dioxide begins to be absorbed by the potassium hydroxide bulbs. Combustion is complete in twenty-five minutes or less. In removing the asbestos from the crucible there is often, when copper solution has been used for dissolving the sample, a black residue remaining where the carbon was, which may mislead the inexperienced, but it is oxide of copper, as is easily proved by its solubility in strong hydrochloric acid.

When the carbon, after filtration, is well washed both with hydrochloric acid and hot water, there is very little chlorine or hydrochloric acid to fear, and the moisture tube effectually stops it. After every five or six combustions, it is only necessary to rinse out the tube with distilled water and connect it again. This moisture tube has been in use in my laboratory for several years, and it has proved itself a simple and efficient means of retaining chlorine and hydrochloric acid. The tube was made for me by Greiner; it is six inches long and three-fourths inch in diameter. The two bulbs are empty; the tube itself is filled with glass beads of about one-eighth inch in diameter. The tube retains about two and a half cc. water when drained. In some experiments an acid solution of silver sulphate was used in place of water, but, under the conditions, it was not more effective than water.

It may be interesting to note here that in some experiments made to determine how near the carbon could be determined by use of the crucible without the cupric oxide tube, it was found, as was of course to be expected, that only about ninety per cent. of the carbon was oxidized to carbon dioxide and determined. Another experiment in which asbestos coated with cupric oxide was placed on top of the carbon in the crucible, without the cupric

oxide tube, gave much better results, but still slightly below the correct figures.

The following are a few carbon determinations :

	By combustion in a porcelain tube in oxygen.	By combustion in air in crucible.	
Steel A	1.035	1.034	1.035 1.039
" B	1.040		1.046
" C	1.032		1.029
" D	0.466		0.466

DUPLICATE RESULTS BY COMBUSTION IN AIR IN CRUCIBLE.

Graphite in pig iron	3.327	3.334
Soft steel E.....	0.026	0.026
" " F.....	0.023	0.023
Steel G.....	0.188	0.187
" H	0.580	0.582

By the kindness of Mr. C. A. Buck, chemist of the Bethlehem Iron Co., I am able to give the following series of carbon results obtained by him while testing the reliability of the combustion apparatus preparatory to using it regularly in the laboratory of the Bethlehem Iron Co. For steels Mr. Buck uses fifteen minutes' combustion and five minutes' aspiration. For pig irons he uses twenty-five minutes' combustion. The results are as follows, on standard samples :

	Combustions in platinum tube.	Combustions in crucible.	Average.
Steel No. 1.....	1.060	1.059 1.058 1.064 1.066 1.060 1.063 1.063	1.062
Steel No. 2.....	0.490	0.491 0.496 0.488 0.493 0.490 0.487 0.488	0.490

	Combustions in platinum tube.	Combustions in crucible.	Average.
Steel No. 3.....	0.183	0.178 0.184 0.189 0.179 0.180	
		<hr/>	0.182
Steel No. 4.....	1.020	1.020 1.020 1.025	
		<hr/>	1.022
Steel No. 5.....	0.700	0.696 0.699	
		<hr/>	0.698
Pig iron No. 1—Total carbon..	3.670		3.690
Pig iron No. 2 " "	3.638	3.600 3.620 3.646 3.620	
		<hr/>	3.622

The crucible may also be used in the determination of carbonic acid and combined water in ores, limestone, etc. For these determinations the apparatus is arranged in the following order: The air passes first through the potassium hydroxide bulbs, then through a calcium chloride tube, then through the crucible containing the dried sample, preferably contained in a small basket of platinum foil fitting closely into the bottom of the crucible. Next to the crucible is the weighed calcium chloride tube and following this the potassium hydroxide bulbs and guard tube of calcium chloride. In determining water, it is necessary to heat the water in the beaker supplying the stopper in order to prevent condensation of moisture on it. Constant weights obtained on the calcium chloride tube with the stopper supplied with hot water agree within 0.0001 to 0.0003 gram, while, with cold water in the stopper, the increase of weight was sometimes as high as 0.0040 gram. The water condensed on the stopper would, to an appreciable extent, be drawn down under the rubber band.

In determining carbonic acid in limestone, one gram of the finely ground sample is placed in the bottom of the crucible and on top of this is placed a layer of ignited asbestos. The ignition

is maintained for a half hour. In determining water alone, there is, after the crucible, only the weighed calcium chloride tube and the guard tube of calcium chloride. The following are some results on carbon dioxide and water.

	Carbon dioxide.		Water.
	I.	II.	
In zinc ore A.....	7.80-7.94		0.60
" " " B.....	1.35		1.12
" " " C.....	7.68		1.22
" " " D.....	1.23-1.21		0.76
" " " E.....	2.76		0.71
" " " F.....	2.58		0.55

Mr. J. W. Louder obtained the following results in determining carbon dioxide and water :

	Carbon dioxide.		
	I.	II.	III.
In limestone A.....	45.80	45.65	45.62
" " B.....	44.29	44.38
	Water.		
	I.	II.	III.
In selenite	20.13	20.12	20.23

The crucible has also been used in determining iron in iron ore by reduction in hydrogen at a red heat, solution of the reduced iron in sulphuric acid and titration with permanganate solution. In the arrangement of the apparatus for this purpose, the hydrogen is passed from the evolution flask through a wash-bottle containing strong sulphuric acid. Then through the crucible containing one-half gram of the dry ore weighed out into a small basket of platinum foil fitting the bottom of the crucible.

The ore should be roasted in air in the open crucible for about five minutes to destroy any carbonaceous matter present. It is allowed to cool and then the stopper is inserted and hydrogen is passed through the apparatus. When all air has been expelled, the crucible is heated to a red heat for one-half hour, allowed to cool perfectly in the hydrogen current, then dissolved in sulphuric acid and titrated. This method, while accurate for ores containing no iron in the insoluble residue, has no advantage over some of the more rapid methods. An Alabama hematite containing 48.36 per cent. total iron (48.24 per cent. soluble in hydrochloric acid, and 0.12 per cent. insoluble in hydrochloric

acid) gave, by reduction in hydrogen, 48.26 per cent. iron, showing complete reduction of all the iron but the small amount present in a combination insoluble in hydrochloric acid. This method is not recommended for general use, but is given merely as an illustration of the widely various uses to which the crucible may be put.

It is, however, not adapted for those organic combustions in which condensable decomposition products are formed. These condense in the cooler upper part of the crucible where they are beyond reach of the temperature necessary to burn them. Probably by mixing such organic compounds with suitable oxidizing material, such combustions might be successfully made, but this is a field that has not yet been investigated.

My last combustion apparatus was made for me by the Baker and Adamson Chemical Co., of Easton, Pa., who also furnished me with a reliable quality of pure rubber bands.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, No. 34.]

THE INFLUENCE OF TEMPERATURE ON THE SPECIFIC ROTATION OF SUCROSE AND METHOD OF CORRECTING READINGS OF COMPENSATING POLARISCOPEs THEREFOR.¹

BY HARVEY W. WILEY.

Received March 9, 1899.

THE influence of temperature on the specific rotation of sucrose has been mentioned by several authors. A partial résumé of the literature on the subject is given by von Lippmann.² A more detailed discussion of the subject is given by Sachs.³ A rather full abstract of previous papers on the subject is given by Sachs, who strangely, however, fails to mention the paper of Andrews on this subject. The early writers with the exception of Dubrunfaut⁴ seem to be unanimously of the opinion that the temperature exerts no notable influence on specific rotation. This is the doctrine announced by Tuschmidt⁵ and

¹ Read before the American Chemical Society and Section C, of the American Association for the Advancement of Science, at Boston Meeting, August, 1898, and before the Third International Congress of Applied Chemistry, Vienna, August, 1898.

² *Chemie der Zuckerarten*, Edition 1895, page 672.

³ *Ztschr. Rübenzuckerind.*, 46, 264.

⁴ *J. prakt. Chem.*, 28, 10.

⁵ *Ztschr. Rübenzuckerind.*, (1870), 649.

Mitscherlich.¹ Sachs also cites the experiments of Wachtel,² who explained the difference in polarization under the influence of temperature by ascribing it to the expansion of the quartz plates of the compensating polariscopes used. This explanation is evidently insufficient, and, as will appear further on, erroneous.

Petrucci and Sachs,³ in 1889, also observed differences in polarization, due to temperature, and these observations were corroborated by Wartze.⁴

The experiments of Sachs were conducted by making the sugar solution at a given temperature and then polarizing it at other temperatures, and also by making up the sugar solution at the same temperature at which it was polarized. As a result of his investigations, he concludes that a solution of practically pure sugar, made up at 17.5° , and polarized at 17.5° , will show a decreased polarization of 0.20° Ventzke, when made up at 25° and polarized at 25° .

The causes of variation in polarizations in the trade were considered in a convention of technical chemists held in Berlin in 1895.⁵

In the United States the first corrections which were employed for variations in polarizations due to temperature were those ascertained by the Office of Weights and Measures of the United States Coast and Geodetic Survey in 1890, and adopted by the commission appointed by the Secretary of the Treasury to prepare regulations for use in the Bureau of Internal Revenue of the Treasury Department. The total correction due to variations in temperature for each degree C., as prescribed by the regulations, was 0.0293° Ventzke for a sugar polarizing 100° Ventzke. This correction was uniformly employed in the Bureau of Internal Revenue, in polarizations for determining the amount of bounty to be paid on domestic sugar in the United States, during the whole time in which the act granting such bounty was in force. It appears, therefore, that the first practical application of a correction for variations in temperature in sugar polarizations was applied in the United States.

¹ *Berl. Acad. Ber.*, (1841), 150.

² *Organ des Central-Verein*, Wien 1878, 42.

³ *Bull. Assoc. Belge Chim.*, 15 Febr., 1889, 112.

⁴ *Deutsche Zuckerind.*, 20 April, 1889.

⁵ *Ztschr. des Vereins für Rübensuckerind.*, (1895), 1, 73.

A painstaking study of the influence of temperature on the polarization of cane-sugar was made by Andrews.¹ As a result of the investigations he deduced the following formula to express the influence of temperature on specific rotation :

$$[a]_D^t = [a]_D^{20} - 0.0114 (t - 20).^2$$

If 66.50 be taken as the mean value for $[a]_D^{20}$ the coefficient of change per degree C. is 0.000171,³ which is somewhat smaller than that obtained by Dubrunfaut; namely, 0.000232.

The formula for calculation used by Andrews was

$$[a]_D^t = \frac{100a}{l \times p \times d'}$$

in which a = angle observed, in degrees ;

l = length of tube, in decimeters ;

p = percentage of sugar, by weight *in vacuo*.

d = specific gravity of the solution at temperature of observation, water at 4° C. being unity.

Dividing the total difference in rotation for different temperatures by the number of degrees of difference in the two sets of experiments conducted by Andrews, we have the following as the variation in the rotation for each degree C. in the two sets of experiments :

Difference per degree in the first set	0.0106
“ “ “ “ second set	0.0122
Mean of the two.....	0.0114

Andrews in his second paper⁴ gives a table showing the factors for computing total variations in polarizations of solutions read at temperatures extending from 10° to 40°, both for direct and quartz compensation polariscopes. The mean factor for instruments without quartz compensation for each degree from 17.5° to 40° is 0.00018, and for quartz compensation instruments is 0.00030. These factors multiplied by 100 show the corrections for each degree of temperature for a pure sugar solution; *vis.*, 0.018 due to change in specific rotating power alone and 0.030 for total correction for quartz compensation instruments. These

¹ *Technology Quarterly*, Mass. Inst. of Technology, 2, May, 1889, 367.

² In Andrews' article the coefficient 0.0114 is given as 0.000114, but the context shows that this displacement of the decimal point is evidently a typographical error.

³ This coefficient is obtained by dividing 0.0114 by 66.5.

⁴ *Technological Quarterly*, May, 1889, 2, 373.

figures are almost identical with those obtained in these investigations and given further on.

Schönrock¹ shows that temperature has a marked influence on the rotatory power of sucrose, which he expresses mathematically by the equation $\frac{d(a)}{dt} = -0.0144$, which may be expressed as follows: $[\alpha]_D^t = [\alpha]_D^{20} - 0.0144 (t - 20)$. By a solution of this equation he shows that the influence of temperature on rotation is one-fourth as great as that due to the change of volume of the liquid.

Landolt² elaborates the formula and shows that the change in polarization on the quartz wedge compensation polariscope, of a pure sugar solution, is equal to 0.065° V. for each degree of temperature. Of this 0.029° V. is due to the change of volume, leaving 0.036° V. due to the influence of temperature on polarization alone. These observations by Schönrock and Landolt were not seen by me until the work, on which this paper is based, was finished.

The recent changes in tariffs in the United States have resulted in a return to the polariscopic methods of ascertaining the percentage of sugar in imported sugars, with a view to levying duty in proportion thereto. I was designated by the Secretaries of the Treasury and Agriculture as chairman of a commission charged with preparing regulations for the control of the polarimetric work in the various ports of entry where sugars were received. It seemed advisable to make a new experimental study of the influence of temperature on the rotatory powers of sugars, especially in relation to the use of compensating polariscopes; *i. e.*, those instruments using a quartz wedge or wedges to restore the displacement of the plane of polarization produced by a sugar solution.

The instrument employed in these researches was a large triple shadow polariscope, double wedge compensation, made with the greatest care for the Department of Agriculture of the United States by Schmidt and Haensch, of Berlin.

The instrument was accompanied by three right-handed unnormal quartz plates, standardized by the Imperial Technical

¹ *Ztschr. für Instrumentenkunde*, 17, June, 1897, 180.

² *Das spezifische Drehungsvermögen*, Edition of 1898, pp. 344 *et seq.*

Institute at Charlottenburg. These plates were independently standardized by myself and my assistant, Dr. G. L. Spencer, in a large Landolt-Lippich monochromatic polariscope made by the firm above mentioned. The values in all cases were either determined at 17.5° , the standard temperature, or calculated thereto by accepted formulas. The values obtained by the three sets of independent observers are given in the following table :

Plate number.	Thickness determined by the Imperial Technical Institute. mm.	Rotation at 17.5° , determined by the Imperial Technical Institute. Angular degrees.	Rotation at 17.5° , determined by H. W. Wiley. Angular degrees.	Rotation at 17.5° determined by G. L. Spencer. Angular degrees.	Value on the Ventzke scale, determined by Schmidt and Haensch. $^{\circ}$ V.
1	1.4927	32.420	32.408	32.418	93.59
2	1.6020	34.777	34.748	34.739	100.36
3	1.2042	26.150	26.105	26.119	75.45

From the data supplied by the Imperial Technical Institute of Charlottenburg, and from the markings of the Ventzke scale by Schmidt and Haensch, the following conclusions are drawn :

(1) The rotation of a quartz plate one mm. in thickness at a temperature of 17.5° C. is equal to 21.7148° .

(2) The angular rotation of a quartz plate one mm. thick corresponds to 62.641 divisions on the Ventzke scale.

(3) One degree circular rotation corresponds to 2.8847 Ventzke scale.

(4) One degree of the Ventzke scale corresponds to 0.3465° angular rotation.

The mean determinations of the three independent observers for the three plates are as follows :

	Angular degrees.
Plate No. 1	32.415°
Plate No. 2	34.755°
Plate No. 3	26.125°

Determining the sugar factors¹ by the marked values of the plates, we get the following relations for the two sets of determinations, the data obtained by Wiley and Spencer being combined and compared with the data obtained from the Imperial Technical Institute of Charlottenburg.

¹ These factors are obtained by dividing each of the mean angular readings of the two series of observations by the marked value of the plate with which the observation was made.

Plate number.	Im. Tech. Institute determination. Angular degrees.	Sugar factor. $1^\circ V =$ angular degrees.	Mean of Wiley and Spencer. Angular degrees.	Sugar factor. $1^\circ V =$ angular degrees.	Marked $^\circ V$.
1	32.420	0.34640 $^\circ$	32.413	0.34633 $^\circ$	93.59
2	34.777	0.34652 $^\circ$	34.744	0.34619 $^\circ$	100.36
3	26.150	0.34659 $^\circ$	26.112	0.34608 $^\circ$	75.45
	Mean	0.34650 $^\circ$	Mean	0.34620 $^\circ$	

We have then as the mean of the three factors obtained by the German authorities for converting angular rotation into degrees Ventzke 0.3465. For the same plates we have for the mean determinations secured by Wiley and Spencer the factor 0.3462. The difference between the two sets of determinations is insignificant, being only 0.0003. If now we use these factors for computing the sugar values of the quartz plates we have the following results from the German standard and from the mean standard as determined by Wiley and Spencer.

Plate number.	German rotation. Angular degrees.	Wiley and Spencer rotation. Angular degrees.	Calculated value of plate (German). $^\circ V$.	Calculated value of plate (Wiley and Spencer). $^\circ V$.	Marked value of plate. $^\circ V$.
1	32.420	32.413	93.564	93.625	93.59
2	34.777	34.744	100.367	100.358	100.36
3	26.150	26.112	75.469	75.425	75.45

It is noticed that the variation of the results calculated from the mean factor from the marked values is very slight.

Being assured thus of the practical accuracy of the instrument employed and the control plates by which it was regulated, it was possible to begin the investigations looking to the determination of the influence of temperature on the specific rotatory power. Advantage was taken of the natural changes in the temperature during the period of investigation, to secure working periods of constant temperatures varying from each other by about 5° from 10° to 20° . Lower temperatures were secured, on the one hand, by conducting the experiments in a cold storage room, and on the other, higher temperatures were secured by means of artificial heat, keeping the atmosphere of the room thoroughly stirred by means of electric fans. In all cases the polariscope was exposed to the temperature of observation long enough to permit the various parts thereof to acquire the ambient temperature; *viz.*, from two to five hours.

For the purpose of having an absolutely unvarying quality of sugar solution, the whole of the material to be used was dissolved at one time into a thick sirup having almost exactly fifty per cent. of pure sugar and fifty per cent. of water. This sirup was preserved by having added to the water before solution an appropriate quantity of mercuric chloride. Double the normal quantity by weight of this solution was used in each determination. One flask, graduated with the greatest accuracy to a true Mohr flask at 17.5° , was used for all the determinations. With these sugars the following recorded observations were made. In each case, unless otherwise noted, five solutions were used and each solution was read four times, or more if there were errant readings, and the mean of the four concordant readings taken as representing the true reading.

In order to secure a better check on the readings, each set of readings was made in triplicate, one set with the white light telescope, one with the yellow light telescope, and one by inserting in the instrument a left-handed quartz plate of known value. The value of the control plate was determined by each of these methods and the necessary corrections made to bring them all up to the same standard of comparison. By adopting this method of triple readings any possible error of observation was eliminated. These triple readings were made in all cases, except the readings at 4° in the cold storage room, where, on account of the low temperature, it was deemed advisable to shorten the work by leaving out one of the sets of readings; *viz.*, the one checked against the left-handed quartz plate.

READINGS AT 4° .

On the afternoon of the 15th of April, 1898, readings were made at 4° in the cold storage room of the Washington Central Market, one of the rooms of which was kindly placed at our disposal by the superintendent.

Five solutions were read with the yellow and white lights. The term "yellow light" hereinafter employed refers to the readings with a telescope carrying a crystal of potassium bichromate or yellow glass plate, or with a tube containing a solution of potassium bichromate. On account of the absence of gas, in

the cold storage rooms, a kerosene lamp was used as the source of light. In all cases the temperature of the instrument and solutions was determined by a delicate thermometer, standardized by the Office of Weights and Measures of the Coast and Geodetic Survey. The readings of the right-handed quartz plate were as follows :

	°v.
With white light	100.20
With yellow light	100.24

The variations in the readings of the standard quartz plates, which will be noticed in the data here and following, aside from the nature of the light, are due to differences in setting the double quartz wedge compensation and not to changes in rotatory power. The readings of the sugar solutions with the yellow and white light were as follows :

Number.	Yellow light. °v.	White light. °v.
1	100.25	100.20
2	100.24	100.20
3	100.19	100.19
4	100.24	100.25
5	100.22	100.21
Means.....	100.23	100.21

Corrections: Add to the reading of the yellow light 0.12. Add to the reading of the white light 0.16.

These corrections here and following represent the differences between the observed reading of the unnormal quartz plate and its marked value; *viz.*, 100.36.

	°v.
Corrected means: Yellow light	100.35
White light.....	100.37
Mean of the two means	100.36

READINGS AT 10°.

On the night of April 14-15, between eleven and two o'clock, the external temperature sank to a little below 10°, and a series of readings was made at 10°. Preliminary readings were as follows :

	°v.
Right-handed plate, white light.....	100.33
Right-handed plate, yellow light	100.33
Right and left plates, white light.....	8.45
Difference in plates.....	91.88

Readings of the sugar solutions with			
	quartz plate. ¹ °v.	yellow light. °v.	white light. °v.
1	100.17	100.15	100.20
2	100.16	100.10	100.18
3	100.16	100.16	100.19
4	100.18	100.15	100.20
5	100.17	100.13	100.20
Means.....	100.17	100.14	100.19

Corrections: Add 0.03 to all mean readings. The corrected mean readings are:

	°v.
Solutions, with quartz plate	100.20
" " yellow light	100.17
" " white light	100.22
Mean.....	100.20

READINGS AT 15°.

A northwestern rainstorm on the morning of April 14 made it easily possible to secure a temperature of 15° in the observation room. A series of readings was therefore made at this temperature. The preliminary readings were as follows:

	°v.
Right-handed quartz plate, with white light.....	100.33
Right-handed quartz plate, with yellow light.....	100.29
Right-handed and left-handed quartz plates together, with white light.....	8.50
Difference between the two plates, 100.33—8.50=91.83.	

To facilitate observations and avoid changing the telescopes for white and yellow lights, a one-fourth per cent. solution of bichromate of potassium was prepared, with which a 100 mm. observation tube was filled and placed in the trough of the instrument, when it was desired to get a reading with yellow light. This gave a beautiful field, clearer than the yellow glass disk, and gave readings superior in every way to those made by means of the yellow light telescope.

Readings of the solutions with			
	quartz plate. °v.	yellow light. °v.	white light. °v.
1	100.02	99.95	100.05
2	100.06	99.95	100.05
3	100.03	99.95	100.04
4	100.10	100.01	100.08
5	100.03	99.93	100.03
Means	100.05	99.96	100.05

¹ The readings entered here and following in column marked "quartz plate" are the observed readings of the solution with left-handed plate plus the difference between the reading of the right- and left-handed plates together. In this case the observed reading of solution No. 1, was 8.29. The reading of the solution is 8.29 + 91.88, the difference between the two plates.

Corrections: Add 0.03 to the readings with the quartz plate and white light telescope, and 0.07 to the readings with the yellow light telescope.

	Corrected means. "v.
Solutions, with quartz plate.....	100.08
" " yellow light	100.03
" " white light.....	100.08
Mean of means.....	100.06

Variation from the mean reading at 20°, 0.18.

READINGS AT 20°.

On the morning of April 13, the temperature of the polariscope room being at 20°, four samples were polarized at the temperature mentioned. The reading of the right-handed plate by the plain telescope was 100.32; by the yellow eye-piece, 100.28. The reading of the two plates by the white light telescope was 8.46, showing the true value of the left-handed plate at the temperature mentioned to be 91.86.

The mean readings of the four samples were as follows:

Readings of sugar solutions with			
	quartz plate. "v.	yellow light. "v.	white light. "v.
1	99.89	99.71	99.86
2	99.87	99.73	99.86
3	99.91	99.75	99.86
4	99.87	99.73	99.86
Means	99.89	99.73	99.86

Corrections: Add 0.04 to the mean reading with the quartz plate and the white telescope. Add 0.08 to the mean reading of the yellow light.

	Corrected means. "v.
Solutions, with quartz plate.....	99.93
" " yellow light.....	99.81
" " white light.....	99.90
Mean of the means	99.88

READINGS AT 25°.

Five solutions were examined on the afternoon of April 12, at a temperature of 25°. This temperature and those following were obtained by artificial heat, the air in the observation room being kept in constant motion by means of electric fans. Every part of the room was thus kept at the same temperature.

Mean reading of right-handed plate, white light.....	"v. 100.30
Mean reading of right-handed plate, yellow light	100.28
Mean reading of right-handed and left-handed quartz.	8.46
Difference to be added, 91.82.	

Readings of solutions with			
	quartz plate. °V.	yellow light. °V.	white light. °V.
1	99.68	99.60	99.63
2	99.72	99.60	99.73
3	99.72	99.60	99.70
4	99.76	99.61	99.71
5	99.73	99.61	99.71
Means	99.72	99.60	99.70

Corrections: Add 0.06 to the reading with the quartz plate and the white light and 0.08 to the reading with the yellow light.

	Corrected means. °V.
Solutions, with quartz plate	99.78
" " yellow light	99.68
" " white light	99.76
Mean of the means	99.74

READINGS AT 30°.

On the afternoon of April 13, observations were made at 30°. The mean results of the readings were as follows:

	°V.
Right-handed quartz plate, white light	100.33
Right-handed quartz plate, yellow light	100.30
Right-handed and left-handed quartz plate, white light	8.50
The value of left-handed plate in terms of right-handed plate	91.83

Reading of sugar solutions. Means of readings with			
	quartz plate. °V.	yellow light. °V.	white light. °V.
1	99.54	99.45	99.55
2	99.53	99.43	99.54
3	99.53	99.44	99.58
4	99.56	99.45	99.60
5	96.54	99.41	99.56
Means	99.54	99.44	99.57

Corrections: Add 0.03 to the readings of the quartz plate and white light, and 0.06 to the mean reading with yellow light.

	Corrected means. °V.
Solutions, with quartz plate	99.57
" " yellow light	99.50
" " white light	99.60
Mean of the means	99.56
Variation from the mean reading at 25°, 0.18.	

READINGS AT 35°.

On the afternoon of April 14, a series of readings was made at 35°. The preliminary readings were as follows:

	°V.
Right-handed quartz plate, white light	100.33
Right-handed plate, yellow light	100.30
Right and left plates, white light	8.50
Difference in plates	91.83

	Readings of sugar solutions with		
	quartz plates. °V.	yellow light. °V.	white light. °V.
1	99.38	99.34	99.38
2	99.42	99.33	99.40
3	99.38	99.33	99.39
4	99.41	99.31	99.41
5	99.39	99.36	99.40
Means	99.40	99.33	99.40

Corrections: Add 0.03 to the mean reading with the quartz plate and that with the white light, and 0.06 to that with the yellow light.

	Corrected Means. °V.
Solutions, with quartz plate	99.43
" " yellow light	99.39
" " white light	99.43
Mean of corrected means	99.42

READINGS AT 40°

On April 15, a series of readings was made at 40° with the following results:

	°V.
Right-handed plate, white light	100.35
Right-handed plate, yellow light	100.31
Right and left plates, white light	8.55
Difference between the two plates	91.80

	Readings of sugar solutions with		
	quartz plate. °V.	yellow light. °V.	white light. °V.
1	99.23	99.18	99.26
2	99.14	99.14	99.21
3	99.20	99.20	99.23
4	99.23	99.18	99.28
Means	99.20	99.18	99.25

Corrections: Add 0.01 to the readings with the quartz plate and white light, and 0.05 to the readings with yellow light.

	Corrected means. °V.
Solutions, with quartz plate	99.21
" " yellow light	99.23
" " white light	99.26
Mean	99.23

SUMMARY OF MEAN POLARIZATIONS FROM 4° TO 40°.

Temperature. Degrees.	Mean polarization. °v.	Differences. °v.
4	100.36	
10	100.20.	0.16
15	100.06	0.14
20	99.88	0.18
25	99.74	0.14
30	99.56	0.18
35	99.42	0.14
40	99.23	0.18

The relations of the data given in this table are best shown by plotting them on cross-section paper. It is seen by this plot, which is appended hereto, that the line intersecting the different points determined by the instrument is practically a straight one. By plotting the line upon cross-section paper, therefore, it is easy to compute the variations for each degree or a fraction of a degree for a sugar polarizing practically 100° in the ordinary conditions secured in the use of the triple-shadow instrument with the Ventzke scale. For sugars of different content of sucrose the magnitude of the corrections to be employed is easily calculated and, for convenience, these corrections are given in the appended table for temperatures from 4° to 40° and for sugar content from 80 to 100 per cent. These data are computed from the points of intersection of the straight line showing the polarization of pure sugar measured by quartz wedges at temperatures from 0° to 40°. These data in extreme cases do not differ more than 0.03 from those determined from the direct observations made. While it is entirely probable that there are slight differences in the rates of change at different temperatures, as shown by the data of observation, for practical purposes, it is better to assume that the rate of change is uniform throughout and therefore is represented by a straight line.

Following is a table of corrections for polarizations made with quartz-wedge compensating polariscopes at temperatures other than the standard temperature of 17.5° C. To obtain the proper correction select the number found at the intersection of the horizontal column corresponding most nearly with the observed polarization, and the vertical column headed with the temperature at which the observation is made. This correction is to be subtracted from the observed polarization when the temperature is below 17.5° C., and added when the temperature of observation is above 17.5° C.

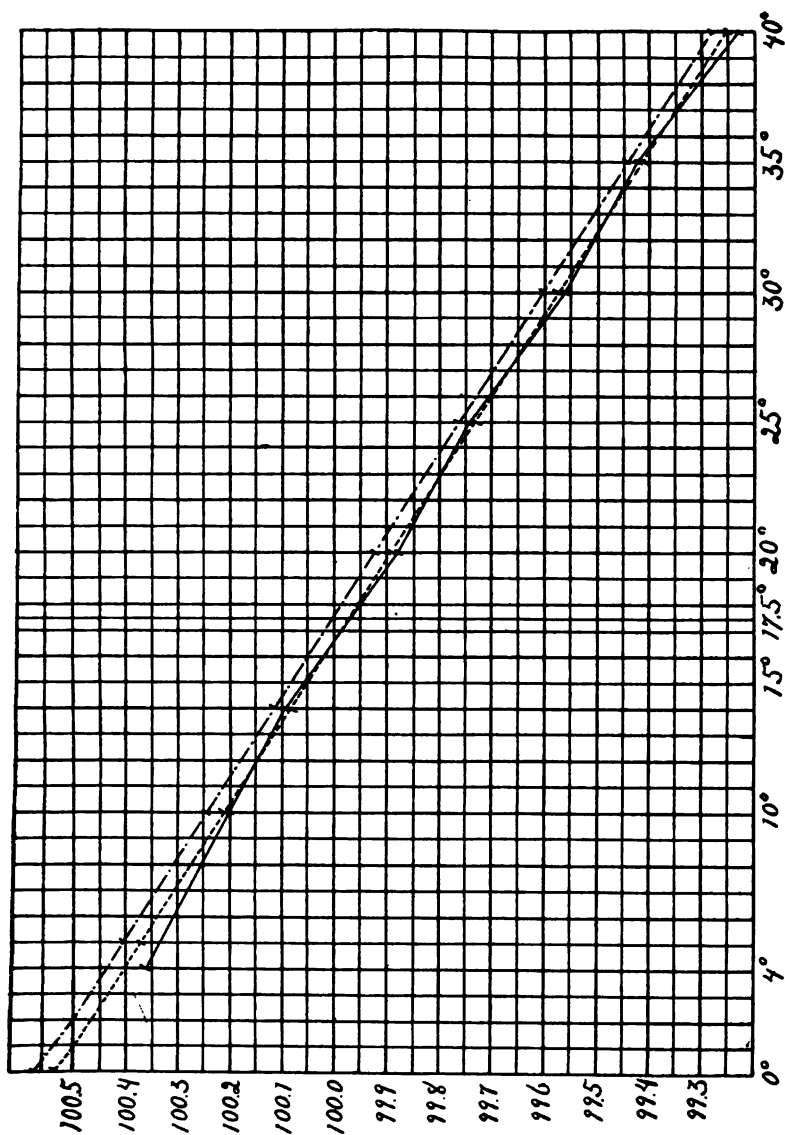
TEMPERATURE, DEGREES CENTIGRADE.

Degrees Veniske. 4	5	6	7	8	9	10	11	12	13	14	15	16	17	17.5	18	19	20	21
100..	0.43	0.40	0.37	0.34	0.30	0.27	0.24	0.21	0.18	0.14	0.11	0.08	0.05	0.00	0.02	0.05	0.08	0.11
99..	0.43	0.40	0.37	0.34	0.30	0.27	0.24	0.21	0.18	0.14	0.11	0.08	0.05	0.00	0.02	0.05	0.08	0.11
98..	0.42	0.39	0.36	0.33	0.29	0.26	0.24	0.21	0.18	0.14	0.11	0.08	0.05	0.00	0.02	0.05	0.08	0.11
97..	0.42	0.39	0.36	0.33	0.29	0.26	0.23	0.20	0.17	0.14	0.11	0.08	0.05	0.00	0.02	0.05	0.08	0.11
96..	0.41	0.38	0.36	0.33	0.29	0.26	0.23	0.20	0.17	0.13	0.11	0.08	0.05	0.00	0.02	0.05	0.08	0.11
95..	0.41	0.38	0.35	0.32	0.29	0.26	0.23	0.20	0.17	0.13	0.10	0.08	0.05	0.00	0.02	0.05	0.08	0.10
94..	0.40	0.38	0.35	0.32	0.28	0.25	0.23	0.20	0.17	0.13	0.10	0.08	0.05	0.00	0.02	0.05	0.08	0.10
93..	0.40	0.37	0.34	0.32	0.28	0.25	0.22	0.20	0.17	0.13	0.10	0.07	0.05	0.01	0.01	0.05	0.07	0.10
92..	0.40	0.36	0.34	0.31	0.28	0.25	0.22	0.19	0.17	0.13	0.10	0.07	0.05	0.01	0.01	0.05	0.07	0.10
91..	0.39	0.36	0.34	0.31	0.27	0.25	0.22	0.19	0.16	0.13	0.10	0.07	0.05	0.01	0.01	0.05	0.07	0.10
90..	0.39	0.36	0.33	0.31	0.27	0.24	0.22	0.19	0.16	0.13	0.10	0.07	0.05	0.01	0.01	0.05	0.07	0.10
89..	0.38	0.36	0.33	0.30	0.27	0.24	0.21	0.19	0.16	0.12	0.10	0.07	0.05	0.01	0.01	0.05	0.07	0.10
88..	0.38	0.35	0.33	0.30	0.26	0.24	0.21	0.18	0.16	0.12	0.10	0.07	0.04	0.01	0.01	0.04	0.07	0.10
87..	0.37	0.35	0.32	0.30	0.26	0.23	0.21	0.18	0.16	0.12	0.10	0.07	0.04	0.01	0.01	0.04	0.07	0.10
86..	0.37	0.34	0.32	0.29	0.26	0.23	0.21	0.18	0.15	0.12	0.09	0.07	0.04	0.01	0.01	0.04	0.07	0.09
85..	0.37	0.34	0.31	0.29	0.26	0.23	0.20	0.18	0.15	0.12	0.09	0.07	0.04	0.01	0.01	0.04	0.07	0.09
84..	0.36	0.34	0.31	0.29	0.25	0.23	0.20	0.18	0.15	0.12	0.09	0.07	0.04	0.01	0.01	0.04	0.07	0.09
83..	0.36	0.33	0.31	0.28	0.25	0.22	0.20	0.17	0.15	0.12	0.09	0.07	0.04	0.01	0.01	0.04	0.07	0.09
82..	0.35	0.33	0.30	0.28	0.25	0.22	0.20	0.17	0.15	0.11	0.09	0.07	0.04	0.01	0.01	0.04	0.07	0.09
81..	0.35	0.32	0.30	0.28	0.24	0.22	0.19	0.17	0.15	0.11	0.09	0.06	0.04	0.01	0.01	0.04	0.06	0.09
80..	0.34	0.32	0.30	0.27	0.24	0.22	0.19	0.17	0.14	0.11	0.09	0.06	0.04	0.01	0.01	0.04	0.06	0.09
79..	0.34	0.32	0.29	0.27	0.24	0.21	0.19	0.17	0.14	0.11	0.09	0.06	0.04	0.01	0.01	0.04	0.06	0.09
78..	0.33	0.31	0.29	0.27	0.23	0.21	0.19	0.16	0.14	0.11	0.09	0.06	0.04	0.01	0.01	0.04	0.06	0.09
77..	0.33	0.31	0.28	0.26	0.23	0.21	0.18	0.16	0.14	0.11	0.09	0.06	0.04	0.01	0.01	0.04	0.06	0.09
76..	0.33	0.30	0.28	0.26	0.23	0.21	0.18	0.16	0.14	0.11	0.08	0.06	0.04	0.01	0.01	0.04	0.06	0.08
75..	0.32	0.30	0.28	0.26	0.23	0.20	0.18	0.16	0.14	0.11	0.08	0.06	0.04	0.01	0.01	0.04	0.06	0.08

TEMPERATURE, DEGREES CENTIGRADE—(Continued).

Degrees Ventric.	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
100..	0.14	0.18	0.21	0.24	0.27	0.30	0.34	0.37	0.40	0.43	0.46	0.50	0.53	0.56	0.59	0.62	0.66	0.69	0.72
99..	0.14	0.18	0.21	0.24	0.27	0.30	0.34	0.37	0.40	0.43	0.46	0.50	0.52	0.55	0.58	0.61	0.65	0.68	0.71
98..	0.14	0.18	0.21	0.24	0.26	0.29	0.33	0.36	0.39	0.42	0.45	0.49	0.52	0.55	0.58	0.61	0.65	0.68	0.71
97..	0.14	0.17	0.20	0.23	0.26	0.29	0.33	0.36	0.39	0.42	0.45	0.49	0.51	0.54	0.57	0.60	0.64	0.67	0.70
96..	0.13	0.17	0.20	0.23	0.26	0.29	0.33	0.36	0.38	0.41	0.44	0.48	0.51	0.54	0.57	0.60	0.63	0.66	0.69
95..	0.13	0.17	0.20	0.23	0.26	0.29	0.32	0.35	0.38	0.41	0.44	0.48	0.50	0.53	0.56	0.59	0.63	0.66	0.68
94..	0.13	0.17	0.20	0.23	0.25	0.28	0.32	0.35	0.38	0.40	0.43	0.47	0.50	0.53	0.55	0.58	0.62	0.65	0.68
93..	0.13	0.17	0.20	0.22	0.25	0.28	0.32	0.34	0.37	0.40	0.43	0.47	0.49	0.52	0.55	0.58	0.61	0.64	0.67
92..	0.13	0.17	0.19	0.22	0.25	0.28	0.31	0.34	0.36	0.40	0.42	0.46	0.49	0.52	0.54	0.57	0.61	0.63	0.66
91..	0.13	0.16	0.19	0.22	0.25	0.27	0.31	0.34	0.36	0.39	0.42	0.46	0.48	0.51	0.54	0.56	0.60	0.63	0.66
90..	0.13	0.16	0.19	0.22	0.24	0.27	0.31	0.33	0.36	0.39	0.41	0.45	0.48	0.50	0.53	0.56	0.59	0.62	0.65
89..	0.12	0.16	0.19	0.21	0.24	0.27	0.30	0.33	0.36	0.38	0.41	0.45	0.47	0.50	0.53	0.55	0.59	0.61	0.64
88..	0.12	0.16	0.18	0.21	0.24	0.26	0.30	0.33	0.35	0.38	0.40	0.44	0.47	0.49	0.52	0.55	0.58	0.61	0.63
87..	0.12	0.16	0.18	0.21	0.23	0.26	0.30	0.32	0.35	0.37	0.40	0.44	0.46	0.48	0.51	0.54	0.57	0.60	0.63
86..	0.12	0.15	0.18	0.21	0.23	0.26	0.29	0.32	0.34	0.37	0.40	0.43	0.46	0.48	0.51	0.53	0.57	0.59	0.62
85..	0.12	0.15	0.18	0.20	0.23	0.26	0.29	0.31	0.34	0.37	0.39	0.43	0.45	0.48	0.50	0.53	0.56	0.59	0.61
84..	0.12	0.15	0.18	0.20	0.23	0.25	0.29	0.31	0.34	0.36	0.39	0.42	0.45	0.47	0.50	0.52	0.55	0.58	0.60
83..	0.12	0.15	0.17	0.20	0.22	0.25	0.28	0.31	0.33	0.36	0.38	0.42	0.44	0.46	0.49	0.51	0.55	0.57	0.60
82..	0.11	0.15	0.17	0.20	0.22	0.25	0.28	0.30	0.33	0.35	0.38	0.41	0.43	0.46	0.48	0.51	0.54	0.57	0.59
81..	0.11	0.15	0.17	0.19	0.22	0.24	0.28	0.30	0.32	0.35	0.37	0.41	0.43	0.45	0.48	0.50	0.53	0.56	0.58
80..	0.11	0.14	0.17	0.19	0.22	0.24	0.27	0.30	0.32	0.34	0.37	0.40	0.42	0.45	0.47	0.50	0.53	0.55	0.58
79..	0.11	0.14	0.17	0.19	0.21	0.24	0.27	0.29	0.32	0.34	0.36	0.40	0.42	0.44	0.47	0.49	0.52	0.55	0.57
78..	0.11	0.14	0.16	0.19	0.21	0.23	0.27	0.29	0.31	0.33	0.36	0.39	0.41	0.44	0.46	0.48	0.51	0.54	0.56
77..	0.11	0.14	0.16	0.18	0.21	0.23	0.26	0.28	0.31	0.33	0.35	0.39	0.41	0.43	0.45	0.48	0.51	0.53	0.55
76..	0.11	0.14	0.16	0.18	0.21	0.23	0.26	0.28	0.30	0.33	0.35	0.38	0.40	0.43	0.45	0.47	0.50	0.52	0.55
75..	0.11	0.14	0.16	0.18	0.20	0.23	0.26	0.28	0.30	0.32	0.34	0.38	0.40	0.42	0.44	0.47	0.50	0.52	0.54

GRAPHIC REPRESENTATION OF THE INFLUENCE OF TEMPERATURE ON THE
ROTATION OF SUCROSE AS DETERMINED BY MEANS OF THE SCHMIDT
AND HAENSCH TRIPLE-FIELD SACCHARIMETER.



The mean readings at the various temperatures of a commercial sugar, polarizing 99.97° Ventzke at 17.5° C., are shown by

The straight line from which the observations, made at temperatures from 10° C. to 40° C., inclusive, differ by only 0.01° Ventzke is shown by

The parallel straight line, representing the polarization of pure sucrose at temperatures from 0° to 40° C. is shown by

The total variation in polarization observed in this series of experiments for the 36° between 4° and 40° was 100.36—99.23, or 1.13° Ventzke, an average difference of 0.0314 for each degree of temperature. A comparison of this result with those of other observers is given in the following table :

Observer.	Variations in the polarization of a pure sugar for each degree centigrade Degree Ventzke.
Andrews	0.0300
U. S. Coast and Geodetic Survey.....	0.0293
Schönrock and Landolt.....	0.0360
Wiley	0.0314
Mean	0.0317

DETERMINATION OF THE CHANGE IN POLARIZATION DUE TO THE INFLUENCE OF TEMPERATURE ON THE SPECIFIC ROTATION, OTHER TEMPERATURE INFLUENCES HAVING BEEN ELIMINATED.

Having thus determined with the greatest exactitude the total variations in polarizations under the influence of temperature, it remains to determine the magnitude of the deviation produced by temperature as a result of change of specific rotatory power of the sugar alone. It is evident that the temperature affects the polarization of a sugar solution in a compensating instrument in the following ways :

(1) By producing variations in the capacity of the flask ; (2) by producing variations in the length of the observation tube ; (3) by producing variations in the degree of concentration ; (4) by changes produced in the rotating power of the compensating quartz wedges ; and (5) by changes produced in the specific rotatory power of the sugar solution itself. It is understood that

the changes due to change of volume of the solution, are not considered here, because the readings are made at the same temperature as those at which the solutions are made.

It is evident, therefore, that if the magnitude of the first four of these factors can be determined, and the total variation in polarization corrected accordingly, the residual quantity of variation must be due to the influence of the temperature upon the specific rotatory power, and an effort will now be made to determine the magnitude of these various factors and to correct the total deviation from the polarization at 17.5° therefor.

(1) *Variations in the Size of the Flask.*—The flask employed in these investigations was most carefully graduated, both in this laboratory and by the Office of Weights and Measures of the Coast and Geodetic Survey, and was found to contain 100.23 cc. at a temperature of 17.5° . It was, therefore, a true Mohr flask, within 0.004 of a cubic centimeter. The variations in the size of the flask due to changes in temperature, calculated by the formula given in the tables of Landolt and Boernstein, are as follows:

Temperatures. C.	Capacities. cc.	Capacities. Mohr cc.
4	100.196	99.966
10	100.211	99.981
15	100.224	99.994
17.5	100.230	100.000
20	100.236	100.006
25	100.249	100.019
30	100.261	100.031
35	100.274	100.044
40	100.286	100.056

(2) *Variations in the Length of the Tube.*—The glass observation tube employed in the investigations had a length of 200 mm. at a temperature of 17.5° . Its length at the other temperatures of observation is shown by the following table:

Temperature. C.	Length. mm.
4	199.976
10	199.987
15	199.996
17.5	200.000
20	200.004
25	200.013
30	200.022
35	200.031
40	200.040

It is evident that the changes in the capacity of the flask and in the length of the tube are, to a certain extent, compensatory. As the flask increases in size, thus diminishing the proportion of the sugar to the volume, the tube increases in length, producing a partial compensation. The rate of increase in the capacity of the flask is, however, slightly greater than in the length of the tube, so that at temperatures varying considerably from 17.5° an appreciable correction is necessary. The amount of this correction is shown in the following table, which gives the variation in the first column of the length of the tube, in the capacity of the flask for each 5° in the second column.

Temperature. °C.	Variation in the length of tube. mm.	Variation in the capacity of flask. cc.
4	0.024	0.034
10	0.013	0.019
15	0.004	0.006
17.5
20	0.004	0.006
25	0.013	0.019
30	0.022	0.031
35	0.031	0.044
40	0.040	0.056

In the comparison of the variations in the capacity of the flask and the length of the tube due to temperature, it should be remembered that 100 cc. are compared with 200 mm. The percentage of variation, therefore, referred to units, is only half as great in the tube as in the flask. In other words, assuming that the capacity of the flask remains constant, it is seen that a variation of one-tenth mm. in the length of the tube produces a variation of only 0.05° in the polarization of the sugar. The variation in the length of the tube, therefore, expressed in millimeters, must be doubled in order to make a direct comparison. When this rule is applied it is seen that the correction for polarization, due to the volume of the flask, is directly proportional to the change in capacity. In other words, at 40° it is seen that the flask has increased 0.056 cc. in capacity. The polarization, therefore, as directly read on the instrument, should be increased by 0.056 to compensate for this increase in volume. On the other hand, we see that at the same temperature the length of the tube is increased by 0.040, and therefore the polarization

must be diminished by just half that amount to reduce it to the proper scale; namely, 0.020. Thus the total correction for the polarization at 40° for changes in the volume of the flask and length of the tube is made in the following way:

Example: Let the polarization at 40° be 99.24; add 0.056 to compensate for change in the volume of the flask and the polarization becomes 99.296. Subtract 0.020 to allow for the increase in the length of the tube, and the polarization becomes 99.276. Applying this principle to the correction of the polarizations obtained upon the standard samples of sugar at the different temperatures, we have the following for the polarizations of sugars for the temperatures named, after correction for changes induced by temperature in the volume of the flask and the length of the tube.

Temperature. C.	Corrected polarizations. ° V.
4	100.338
10	100.188
15	100.056
20	99.884
25	99.753
30	99.580
35	99.449
40	99.266

DERIVATION OF A FORMULA FOR COMPUTING THE CORRECTION FOR THE INCREASE IN THE CAPACITY OF THE FLASK AND FOR THE INCREASE IN THE LENGTH OF THE TUBE WHEN THE OBSERVATION IS MADE AT ANY TEMPERATURE OTHER THAN THE STANDARD TEMPERATURE OF 17.5°.

Let the observed polarization at this temperature be 99.23° V; the capacity of the flask 100.056 Mohr cc. (1 Mohr cc. = 1.00234 true cc.); and the length of the tube 200.040 mm.

The number of grams of sugar per 100 cc. (Mohr) of the solution is

$$100.056 : 100 :: 26.048 : x$$

$$x = \frac{100 \times 26.048}{100.056} = 26.0334.$$

The true polarization of a solution containing x grams of sugar per 100 cc. (Mohr) and giving a reading of 99.23 is

$$x : 26.048 :: 99.23 : y.$$

Then the polarization corrected for the expansion of the flask,

$$y = \frac{26.048 \times 99.23 \times 100.056}{100 \times 26.048} = 99.286.$$

This value must now be corrected for the increased length of the tube, by the following ratios:

$$200.040 : 200 :: 99.286 : z.$$

Then the polarization corrected for the expansion of the flask and the tube is,

$$z = \frac{200 \times 99.286}{200.040} = 99.266.$$

Substituting the unreduced fractional value of y in the last proportion, we have:

$$200.040 : 200 :: \frac{26.048 \times 99.23 \times 100.056}{100 \times 26.048} : z.$$

$$z = \frac{200 \times 26.048 \times 99.23 \times 100.056}{200.040 \times 100 \times 26.048},$$

or dropping out the common factor 26.048, which occurs in both numerator and denominator, the expression becomes

$$z = \frac{200 \times 99.23 \times 100.056}{200.040 \times 100}.$$

If we let the capacity of the flask at 17.5° be represented by C ; the capacity of the same flask at t degrees by C' ; the length of the tube at 17.5° by l ; the length of the same tube at t degrees by l' ; and the polarization at t degrees by P' ; we have the following general formula:

P' , the polarization corrected for expansion of the flask and observation tube = $\frac{lP'C'}{l'C}$.

Example: A solution polarizes 100.360 under the following conditions:

$$t = 4^\circ \text{ C.}$$

$$l = 200.$$

$$l' = 199.976.$$

$$C = 100.$$

$$C' = 99.966.$$

Then

$$P = \frac{200 \times 100.36 \times 99.966}{199.976 \times 100} = 100.338.$$

VARIATION IN CONCENTRATION.

Perhaps there is no point connected with the polarization of sugars in which scientific literature contains more contradictory statements than that which relates to the influence of concentration on the specific rotatory power. It is not possible here to enter into a discussion of this subject, a matter which will be reserved later on for a separate investigation. It is sufficient here to call attention to the latest summary of our knowledge on this subject contained in Dr. Landolt's work entitled "*Das optische Drehungsvermoege*n, etc.," second edition, page 419. The conclusion which Landolt reaches from a study of the data at hand is as follows: "The specific rotatory power of sucrose for sodium light for all degrees of concentration below 30° may be taken as $[\alpha]_D^{25} = 65.5$." It is evident that the sugar with which the analytical data contained in this paper were obtained was practically pure, since under all the necessary conditions of polarization at 17.5° it gave a reading of 99.97. It is certain that the degree of concentration of the solutions changed with each degree at which the polarizations were made. For instance, in filling the flask at 4°, the quantity of water used was considerably greater by weight than when the flask was filled at 40°. The weight of sugar in all cases having remained the same, it is evident that the degree of concentration of the solution at 4° was considerably less than at 40°. Since, however, as we have just seen, there is practically no correction to be made for variations in concentration under 30 per cent., the influence of this slight difference in concentration may be absolutely eliminated from the calculation. It is established, therefore, that none of the variation noticed in polarization was due to differences in concentration.

CHANGES IN COMPENSATING POWERS OF THE QUARTZ WEDGES.

It is well known that the power of quartz, of a given thickness, of rotating a plane of polarized light, varies with the temperature. As the temperature rises the rotating power of the quartz increases. The rate of increase has been calculated by physicists, and the formula of Joubert is one which is

usually accepted for the purpose of determining the rotating values at different temperatures. This formula is

$$A_t = A_0 (1 + 0.000149t),$$

in which A_0 represents the rotating power of the quartz plate at a temperature of 0° , and A_t represents the rotatory power at any desired temperature. In this formula A may either represent degrees Ventzke or degrees of angular rotation.

E. Gumlich¹ has made careful determinations of the temperature coefficient of quartz for rays of different wave-lengths. He concludes that the influence of temperature on the rotatory power of quartz does not vary materially for light having wave-lengths varying from $656 \mu\mu$ to $436 \mu\mu$. For temperatures from 0° to 100° he expresses the influence of temperature on the specific rotatory power of quartz by the following equation $\phi' = \phi^\circ (1 + 0.000131t + 0.000000195t^2)$.

Using this formula for calculating the value at 40° of a thickness of quartz which rotates 1° V. at 17.5° the value 1.00319 is obtained instead of 1.00335 as given in the table.

Substituting this value in the calculation of the mean corrected polarization obtained at 40° and in the calculation of the specific rotatory power of sucrose at 40° , the numbers 99.582 and 66.288 are obtained, respectively. The former number differs by 0.016° V. from the one given in the table, while the value for $[\alpha]_D^{40}$ is 0.011 less than the result previously noted. It is therefore evident that the use of the formula of Gumlich would not materially change the results reported in this paper.

Applying Joubert's formula to the investigation in question, we have the following data:

A thickness of quartz, which gives a rotation of 1° V. at 17.5° , produces at other temperatures the amount of rotation shown in the following table:

Temperature. °C.	Rotation. °V.	Difference from 17.5°
4	0.99799	0.00201
10	0.99888	0.00112
15	0.99963	0.00037
17.5	1.00000	0.00000
20	1.00037	0.00037
25	1.00112	0.00112
30	1.00186	0.00186
35	1.00261	0.00261
40	1.00335	0.00335

¹ Wiedemann's *Ann. phys. Chem.*, 59, 333; *Ztschr. des Vereins der deutschen Zuckerind.*, (1898), 11, 971-992.

If the compensating system of a polariscope be warmed to 40° C., the quartz wedge used in its construction rotates 1.00335 times the number of degrees Ventzke shown by a quartz of equal thickness at 17.5°.

The true polarization of a sugar solution which reads 99.266° V. at 40° C. (correction having been made for the change in the volume of the flask and in the length of the observation tube, due to change of temperature), is 99.266×1.00335 , or 99.598° V.

Correcting all the results given on page 587, we have :

POLARIZATION OF THE SUGAR UNDER EXAMINATION AT TEMPERATURES FROM 4° TO 40° C.

(Corrections having been made for the changes caused by temperature in the volume of the flask, in the length of the observation tube and in the rotatory power of the quartz used in the construction of the instrument.)

Temperature. °C.	Polarization. °V.
4	100.136
10	100.075
15	100.019
17.5	99.970
20	99.921
25	99.864
30	99.765
35	99.708
40	99.598

If the polarization at t degrees of a thickness of quartz which reads 1° V. at 17.5°, be designated by Q' , we may extend the formula for P' given above, as follows :

P' , the polarization in degrees Ventzke, corrected for changes due to temperature in the volume of the flask, in the length of the observation tube and in the rotatory power of the quartz of the compensating system of the instrument,

$$= \frac{lP'C'Q'}{l'C} ; \text{ in which}$$

l = length of the observation tube at 17.5° C.

t = " " " " " " the temperature of observation.

C = capacity of the flask at the temperature of observation.

Q' = polarization at t of a thickness of quartz reading 1° V. at 17.5°.

P' = observed polarization, degrees Ventzke.

C = capacity of the flask at 17.5° C.

Example :

Let $t = 40^\circ$.

$$P' = 99.24.$$

$$l' = 200.040.$$

$$C' = 100.056.$$

$$Q' = 1.00335.$$

$$l = 200.$$

$$C = 100.$$

$$P'' = \frac{200 \times 99.23 \times 100.056 \times 1.00335}{200.040 \times 100} = 99.598.$$

It is evident, from an inspection of the above data, that a less thickness of the quartz wedge is required to compensate for the rotation produced in the plane of polarized light by a sugar solution at a higher than at a lower temperature. The result of this is that the apparent reading of the solution is lower than the true reading as the temperature of the quartz wedge and its rotating power increase.

CHANGES DUE TO PRESSURE ON THE QUARTZ PLATES AND WEDGES.

It is well known that any strain or pressure exerted on a piece of quartz will change its rotating power. Hence the operator must assure himself that he is using an instrument in which the rotating power of the quartz wedges and quartz plates is not changed by pressure due to changes in temperature. In the double compensating polariscope, used in these investigations, there are four quartz wedges, with independent settings. Theoretically the reading of a quartz plate mounted in such a way as to undergo no pressure, due to changes of temperature, by four quartz wedges, all independently mounted in the same way, should be practically the same at all temperatures. The permissible variations are due only to displacement of the zero mark, which is very common in double compensating instruments, to the personal errors of reading, which may amount to 0.10° V. and to changes in the nature or intensity of light.

The doctrine of probabilities would practically preclude the occurrence of a state of affairs in which the pressure exerted on a mounted quartz plate would be exactly compensated for by the sum of the pressures exerted on four independently mounted quartz wedges.

If in these conditions the readings of a quartz plate at widely varying temperatures in a double compensating instrument, agree within the limits of error above pointed out, it is a convincing proof, that neither the plate nor the wedges have suffered any change in rotating power due to pressure.

I will now compare the readings of the urnormal quartz plate used for control in these investigations, at the various temperatures employed, excluding those made at 4° , in which a different light was used.

READING OF URNORMAL QUARTZ PLATE AT DIFFERENT TEMPERATURES.

Temperature. C.	Reading. V.	Difference.
10	100.33	...
15	100.33	0.00
20	100.32	0.01
25	100.30	0.02
30	100.33	0.03
35	100.33	0.00
40	100.35	0.02

The remarkable uniformity of the readings of the urnormal plate, at such widely varying temperatures, proves beyond any reasonable doubt that none of the data obtained was influenced in any way by pressure exerted either on the quartz plate or wedges.

We find, therefore, the total difference due alone to change in specific rotatory power for 36° equal to 0.538° V., and for 1° 0.01494° V. It therefore appears that for each change of one degree in the temperature the polarization of a pure sugar on an instrument with a Ventzke scale suffers a change of 0.01494° , due exclusively to the change in the specific rotatory power of the sugar solution. Converting this into angular degrees by multiplying by the factor 0.3462, we get the magnitude of the change in specific rotatory power in angular measure due to each degree of change of temperature = 0.005172 . It is now possible to convert the readings obtained on the Ventzke scale into angular measurement and to compute the specific rotatory power for each of the temperatures at which the observations were made. These calculations have been made and the results are found in the following table :

SPECIFIC ROTATORY POWER OF SUCROSE AT TEMPERATURES RANGING
FROM 4° TO 40° C.¹

Temperature of observation. °C.	Readings on Ventzke Scale. ² °V.	Equivalent angular degrees with sodium light.	$[a]_D'$	Differences.		
				Range of temperature. °C.	For whole range.	For 1° C.
4	100.136	34.667	66.657	4 to 10	0.040	0.00667
10	100.075	34.646	66.617	10 " 15	0.038	0.00760
15	100.019	34.627	66.579
17.5	99.970	34.610	66.547	15 " 20	0.065	0.01300
20	99.921	34.593	66.514	20 " 25	0.038	0.00760
25	99.864	34.573	66.476	25 " 30	0.066	0.01320
30	99.765	34.539	66.410	30 " 35	0.038	0.00760
35	99.708	34.519	66.372	35 " 40	0.073	0.01460
40	99.598	34.481	66.299

This weight of sugar in 100.23 true cc. is equivalent to 26.004 grams (weighed *in vacuo*) in 100 true cc.

The formula for specific rotatory power is

$$[a]_D' = \frac{100 a}{lc}.$$

$$[a]_D' = \frac{100 a}{2 \times 26.004} = aC, \text{ when } C = \text{the constant, } \frac{100}{2 \times 26.004}.$$

The specific rotatory power for a given temperature may be calculated directly from the reading of the saccharimeter at the given temperature by the use of the following formula:

$$[\alpha]_D' = \frac{0.3462 P' V' Q'}{26.0639 l'}.$$

0.3462 = the value in angular degrees of 1° V.

P' = the observed polarization, degrees Ventzke.

V' = the capacity of the flask at the temperature of the observation, expressed in true cc.

Q' = the value in degrees Ventzke at t° of the thickness of quartz which gives a rotation of 1° V. at 17.5° C.

l' = the length of the observation tube in decimeters at the temperature of the observation.

26.0639 = the weight in grams (weighed *in vacuo*) of sugar contained in the quantity of the solution prepared.

¹ The observations were made with a triple-field saccharimeter, the readings being converted to angular degrees by use of the factor 0.3462. The concentration was 26.004 grams (weighed *in vacuo*) sugar in 100 true cc. (26.048 grams weighed in air in 100 Mohr cc).

² Corrected for all variations except in specific rotation.

Example : A solution of 26.048 grams of sugar (weighed in air) prepared at 40° C. in a flask that holds 100.23 true cc. at 17.5° C., polarizes 99.23° V. at 40° C.

This solution contains 26.0639 grams of sugar (weighed in vacuo).

$$\begin{array}{rcl}
 \log 0.3462 & = & 9.5393271 \\
 \log P' = \log 99.23 & = & 1.9966430 \\
 \log V' = \log 100.286 & = & 2.0012403 \\
 \log Q' = \log 1.00335 & = & 0.0014525 \\
 \text{colog } 26.0639 & = & 8.5839606 \\
 \text{colog } P' = \text{colog } 2.0004 & = & 9.6988832 \\
 \hline
 \log [\alpha]_{17.5}^{\text{D}} & = & 1.8215067 \\
 [\alpha]_{17.5}^{\text{D}} & = & 66.299^{\circ}
 \end{array}$$

From the foregoing data it is seen that the temperature has a marked effect upon the specific rotatory power of sucrose. After having obtained a large number of readings on a most delicate polariscope in which the conditions of temperature were most carefully controlled, it has been possible to estimate the magnitude of this change in rotatory power. It is seen that the specific rotatory power of the sugar employed at 17.5° is 66.547, and at the extreme ranges of temperature which were reached in the investigation, we find that the specific rotatory power at 4° of the same sugar is 66.657, and at 40°, 66.299. It is thus seen that the specific rotatory power of the sucrose solution increases as the temperature falls, and decreases as the temperature rises, and the mean magnitude of the variation for each degree is 0.00994.

A comparison of this result with those of other observers is given in the following table :

Observer.	Mean changes in the specific rotatory power of su- crose per °C.
Andrews	0.01140
Schönrock	0.01440
Wiley	0.00994
Mean	0.01191

It appears from the results of the investigation that the mean rate of increase is not the same at every temperature, as for instance, it appears to be greater from 15° to 17.5°, from 20°

to 25° , and from 30° to 35° than it is at the other points at which the observations were made. Numerous series of observations, however, would be necessary, on account of the small magnitudes involved, to definitely determine this question.

My thanks are due to Mr. W. H. Krug, who assisted me in obtaining all the experimental data given in this paper, and who cheerfully endured the fatigue and discomfort of working for several nights at very low temperatures; to Mr. E. E. Ewell, who assisted in calculating the data and in constructing the graphical charts and tables of correction; and to Mr. G. L. Spencer, who independently determined the values of the normal quartz plates used in controlling the polarizations.

THE DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC SUBSTANCES CONTAINING NITROGEN.

By O. F. TOWER.

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IN determining carbon and hydrogen in substances containing nitrogen, use is commonly made of a metallic copper spiral at the exit end of the combustion tube to reduce oxides of nitrogen. Liebig was the first to observe that such oxides might be formed, and he showed that the amount of nitric oxide formed, when determining nitrogen by heating with copper oxide, was sufficient to vitiate the results.¹ He further showed that no appreciable quantities of other oxides of nitrogen could be formed, for when the quantity of nitrogen collected was increased by the amount of nitrogen in the nitric oxide produced, the correct percentage of nitrogen in the substance was obtained. Later Klingemann² determined the amount of nitric oxide formed from a variety of complex nitrogen-containing substances, when nitrogen is determined by burning with copper oxide according to the method of Frankland and Armstrong. His results show that the quantity of nitric oxide produced is usually very small, from 0.00 to 0.28 cc., occasionally it is more, and in the case of picric acid 0.90 cc. was found. This last equals only 0.0011 gram. The amount of the substance burned was commonly about 0.1 gram. His results show further that the amount of

¹ *Pogg. Ann.*, 18, 357.

² *Ber. d. chem. Ges.*, 22, 3064.

nitric oxide formed does not depend on the nature of the substance, nor on the percentage of nitrogen in the substance, and, moreover, it is very variable for different combustions of the same substance. It, however, seems to be somewhat influenced by the rapidity of the combustion. No direct determinations of the amount of nitrogen oxidized seems to have been made in connection with the determination of carbon and hydrogen in substances containing nitrogen. A few combustions of such substances, made at the time work on a former article¹ was in progress, seemed to show that no appreciable quantities of oxides of nitrogen could be formed, and that, consequently, a metallic copper spiral was unnecessary, particularly in the case of those substances where the nitrogen was in the amidic form. The following work was, therefore, undertaken to determine, if possible, if oxides of nitrogen are formed in such quantity as to interfere with the accuracy of the determinations of carbon and hydrogen, rendering imperative the use of a metallic copper spiral when burning all such compounds.

The method of making combustions differed somewhat from that described in the article just cited. No cylinder of compressed oxygen was at my disposal in this laboratory, so that it was necessary to use oxygen prepared in the usual manner and confined in a gas-holder over water. For reasons which will be given later, at the close of most of the combustions the oxygen was swept out by air. The series of absorbing tubes was changed slightly by introducing after the first soda-lime tube a small U-tube containing glass wool drenched with sulphuric acid instead of the tube containing in one side soda-lime and in the other calcium chloride. This change was made for the reason that occasionally a carbon determination came out low. It has been shown by Dibbits² that calcium chloride at ordinary temperature fails to absorb about eight per cent. of the water vapor necessary to saturate the air at the same temperature. In cases where combustions are carried on in an atmosphere of oxygen, so that only a small quantity of gas, comparatively, is aspirated through the system of tubes, the error thus caused is usually small enough to be inappreciable. Where, however, the oxy-

¹ This Journal, *21*, 389.

² *Ztschr. anal. Chem.*, *15*, 148.

gen is afterwards displaced by air, and consequently the quantity of gas which passes through the system is much greater, a considerable error can result. With this arrangement of tubes there was no certain means of telling when the absorptive power of the soda-lime tube was exhausted. Hence no soda-lime tube was used for more than two combustions.

The substances burned were selected so as to represent different types of bodies containing nitrogen. They were hippuric acid, paratoluidine, urea, dinitrobenzene, nitraniline, and picric acid. Among these are compounds containing amido and nitro groups, some having a large and some a small percentage of nitrogen. The results obtained with the first five will be given first, and afterwards picric acid will be discussed by itself. Only well-crystallized samples of these preparations were employed. Their purity was established by determining the percentage of nitrogen which they contained. All nitrogen determinations were made according to the Kjeldahl method modified to include the nitrogen of nitrates, as adopted by the Association of Official Agricultural Chemists.¹ The determinations were made in duplicate and resulted as follows:

Substance.	Nitrogen.		Theoretical.
	Found.	Found.	
	1.	2.	
	Per cent.	Per cent.	Per cent.
Hippuric acid.....	7.85	7.82	7.82
Paratoluidine	13.05	13.19	13.08
Urea.....	46.58	46.69	46.67
Dinitrobenzene.....	16.62	16.65	16.67
Nitraniline.....	20.33	20.28	20.29

The agreement between the results obtained and the theoretical is such as to show that the substances were sufficiently pure.

The carbon and hydrogen in these compounds was then determined, sometimes using and sometimes without using a copper spiral. If oxides of nitrogen were formed, and no copper spiral were used, these oxides would pass over and, with the exception of nitric oxide, be absorbed in great part by the concentrated sulphuric acid, thereby increasing the apparent weight of absorbed water, and the corresponding percentage of hydrogen. In the first few combustions, in fact, the percentage of hydrogen

¹ Methods of Analysis, Bulletin 46. Division of Chemistry. U. S. Department of Agriculture, p. 17.

was too high, whether or not a copper spiral were used. For example, from the combustion of dinitrobenzene, the following percentages of hydrogen were obtained :

	Per cent.
With copper spiral	2.84
" " " 	2.62
" " " 	2.66
Without copper spiral	2.69
" " " 	2.54
" " " 	2.75
Theoretical.....	2.38

The inference from these results seemed to be that something rendered the copper spiral ineffective. At the beginning of each of these combustions the tube was filled with oxygen gas, and it was noticed that when a metallic copper spiral was introduced, as it became heated it was immediately oxidized. It is possible that the oxidation was so complete as to prevent the copper having any reducing effect on oxides of nitrogen. To obviate this, at the close of each combustion the oxygen in the tube was swept out by air in the usual manner. With this precaution it could easily be observed that the copper spiral was not oxidized so rapidly as before. The percentage of hydrogen was, however, still too high, varying little from the former results.

In all these combustions the percentage of carbon found was constant and agreed well with the theory. Blank tests at this time showed that the drying train was inadequate, admitting water into the combustion tube. Nothing, therefore, could be inferred from the foregoing results. The sulphuric acid in the drying cylinders was replenished and the number of cylinders increased to three. No further difficulty was then experienced in freeing the entering gases from water. Further combustions now gave a lower percentage of hydrogen, but in the case of substances containing very little hydrogen the results were still somewhat higher than the theory ; no higher, however, than is frequently the case in elementary analysis of compounds of this kind. The results are given below. To avoid the possibility of the copper spiral becoming immediately oxidized and thus proving ineffective, the oxygen was in every case swept out with air.

Substance.	Copper spiral.	Amount used.	Amount CO ₂ found.	Carbon Found.	Carbon Theor.	Amount H ₂ O found.	Hydrogen Found.	Hydrogen Theor.
		Gram.	Gram.	Per cent.	Per cent.	Gram.	Per cent.	Per cent.
Hippuric acid..	with	0.2017	0.4464	60.37	60.34	0.0915	5.08	5.03
	"	0.2057	0.4558	60.31	0.0937	5.10	...
	without	0.1895	0.4176	60.11	0.0860	5.08	...
	"	0.2045	0.4521	60.30	0.0937	5.13	...
	"	0.2032	0.4485	60.21	0.0930	5.12	...
Paratoluidine .	without	0.1912	0.5498	78.44	78.50	0.1452	8.50	8.41
	"	0.1821	0.5242	78.52	0.1369	8.41	..
Urea.....	with	0.2011	0.1472	19.97	20.00	0.1210	6.73	6.67
	"	0.2031	0.1490	20.01	0.1243	6.85	...
	"	0.2119	0.1565	20.15	0.1291	6.82	...
	without	0.2028	0.1487	20.00	0.1240	6.84	...
	"	0.2116	0.1560	20.11	0.1288	6.81	...
	"	0.2006	0.1471	20.00	0.1204	6.72	...
	"	0.2052	0.1498	19.91	0.1245	6.79	...
Dinitrobenzene.	with	0.2194	0.3444	42.82	42.86	0.0482	2.46	2.38
	"	0.2200	0.3467	42.98	0.0496	2.42	...
	without	0.2161	0.3400	42.92	0.0486	2.52	...
	"	0.2108	0.3311	42.84	0.0446	2.37	...
Nitraniiline	"	0.1750	0.3348	52.19	52.17	0.0702	4.49	4.35
	"	0.1782	0.3412	52.23	0.0701	4.40	...

On comparing the results with and without the use of a copper spiral, there is no ground for assuming the formation of oxides of nitrogen. These results were not, however, considered sufficient proof that no such oxides are formed.

As was stated before, any such oxides, with the exception of nitric oxide,¹ would be retained by concentrated sulphuric acid. The sulphuric acid in the first U-tube was, therefore, examined for nitrogen by the Kjeldahl process. The solution of hydrochloric acid used in this work was approximately seminormal, ten cc. containing 0.1845 gram pure acid. The standard ammonia solution was about one-sixth the strength of the acid, ten cc. being equivalent to 0.01200 gram nitrogen. The ammonia solution gradually became weaker on standing, so that its strength in terms of the standard acid was determined each day it was used. Blank determinations were first made to see if the reagents employed were free from nitrogen. Four cc. hydrochloric acid were used in each determination, and the titrations with ammonia were 23.30, 23.18, 23.10, and 23.26 cc., respect-

¹ Nitric oxide is not absorbed by concentrated sulphuric acid. See *J. Soc. Chem. Ind.*, 1885, 178; *Ber. d. chem. Ges.*, 18, 1391; *Chem. News*, 55, 28.

ively, average 23.21 cc. Had the reagents contained no nitrogen, the quantity of ammonia required in each case would be 23.70 cc., which differs from the average by 0.49, or in round numbers 0.50 cc., equivalent to 0.0006 gram nitrogen. Allowance was made for this in all the following determinations. The sensitiveness of the method can also be seen from the above figures. The greatest difference between any two titrations is 0.20 cc., equivalent to 0.00024 gram nitrogen, and the greatest variation from the average is 0.11 cc., equivalent to 0.00013 gram nitrogen. By this method, therefore, nitrogen can be determined within 0.0002 gram. This is sufficiently accurate for this work, as the limit of error in weighing a U-tube under changing atmospheric conditions is usually not less than 0.0002 gram. Simple U-tubes were used to absorb the water and not those of the Volhard pattern with a bulb on one arm, as it was desired that all water should be taken up directly by the sulphuric acid. The U-tubes were filled with some of the same acid as that used for the Kjeldahl determinations. After a combustion the contents of these tubes were poured into a digestion flask, and the tubes well rinsed with additional sulphuric acid. The amount of nitrogen in the acid was then determined.

The sulphuric acid used to absorb the water in most of the combustions, whose results are given in the last table, was treated thus, but no traces of nitrogen could be found. This was surprising, for it was confidently expected that not negligible quantities of nitrogen were oxidized, particularly in the case of nitro bodies, as nitraniline and dinitrobenzene. Several combustions were then made with these two substances, using the same sulphuric acid to absorb the water from two, and sometimes from three, separate combustions. This acid was then examined for nitrogen, but none was found. Soda-lime will absorb all oxides of nitrogen except perhaps nitric oxide.¹ If, therefore, any of the other oxides of nitrogen should escape absorption by the sulphuric acid, they would certainly be absorbed by the soda-lime. The soda-lime which had been used in several combustions of nitraniline and dinitrobenzene was, consequently, treated with concentrated sulphuric acid in a flask,

¹ Nitric oxide is not absorbed by strong alkalies. See *J. Chem. Soc.*, (1877), 2, 37; Wien: *Monatshefte*, 13, 86.

and the mixture distilled until sulphuric acid commenced to come over. This distillate was examined for nitrogen, but none was found. The results of all these determinations were very similar to those obtained in the blank tests. An example will suffice.

SUBSTANCE BURNED, DINITROBENZENE.

	cc.
Hydrochloric acid used in each case.....	3.00
Theoretical amount of ammonia to neutralize, allowance being made for nitrogen in reagents.....	17.40
Actual amount of ammonia used in each titration (substance examined for nitrogen):	
Sulphuric acid from one combustion.....	17.48
" " " two combustions.....	17.37
" " " three combustions.....	17.50
Distillate from soda-lime, two combustions	17.42

In other cases titrations were obtained running from 17.32 to 17.50 cc., the former being the lowest figure ever observed, so that it is safe to draw the inference, that no appreciable quantities of oxides of nitrogen which are absorbed either by concentrated sulphuric acid or soda-lime were formed.

Small quantities of nitric oxide may have been formed, as this gas would pass the sulphuric acid and soda-lime without being absorbed, and consequently would not affect the determinations of carbon and hydrogen. Of course, if it came in contact with oxygen in the tube, it would immediately become oxidized, and then could be readily absorbed. In making a combustion there was, however, little opportunity for oxidation. At the beginning of a combustion the tube was full of air. During the preliminary heating of the substance no air or oxygen was aspirated through the system, so that the oxygen of the contained air would very soon either be used up or driven out by the production of carbon dioxide and other gases. Only after the substance was completely charred and there was no further bubbling of gas through the sulphuric acid of the water-absorbing tube, was the aspiration of oxygen commenced. From Klingemann's results it would be inferred that some nitric oxide might be formed, but in any event very little. It may be remarked that no red fumes were ever noticed where the unabsorbed gases

finally escaped into the air, although under somewhat different circumstances such fumes have been observed by others.¹

The results with picric acid will now be given. With this substance Klingemann² obtained much more nitric oxide than with any other substance which he used.

DETERMINATION OF CARBON AND HYDROGEN IN PICRIC ACID.

Theoretical values, carbon 31.44 per cent., hydrogen 1.31 per cent.

Combustion number.	Copper spiral.	Amount used. Gram.	Amount carbon dioxide found. Gram.	Corresponding carbon. Per cent.	Amount water found. Gram.	Corresponding hydrogen. Per cent.
1	with	0.1551	0.1793	31.53	0.0208	1.50
2	"	0.1551	0.1786	31.41	0.0201	1.45
3	without	0.1605	0.1875	31.86	0.0250	1.75
4	"	0.1613	0.1894	32.03	0.0266	1.85
5	"	0.1512	0.1771	31.95	0.0210	1.55
6	"	0.1614	0.1881	31.79	0.0244	1.69
7	"	0.1595	0.1866	31.91	0.0229	1.61

DETERMINATION OF NITROGEN IN THE SULPHURIC ACID AND SODA-LIME USED IN THE PREVIOUS COMBUSTIONS.

Hydrochloric acid used each time 3.00 cc., equivalent to 17.40 cc. ammonia.³

Combustion number.	Sulphuric acid.			Soda-lime distillate.		
	Titration. cc.	Difference. cc.	Nitrogen. Gram.	Titration. cc.	Difference. cc.	Nitrogen. Gram.
2	17.35	17.42
3	16.85	0.55	0.0007	17.05	0.35	0.0004
4	16.30	1.10	0.0013	16.75	0.65	0.0008
5	17.25	0.15	0.0002	16.90	0.50	0.0006
6	17.20	0.20	0.0002	16.55	0.85	0.0010
7	17.22	0.18	0.0002			

From the first table it will be seen that the results, when no copper spiral was used, not only in almost every case are higher than the results with the copper spiral, but they also do not agree so well with the theory. The second table shows that some nitrogen was found both in the sulphuric acid and in the soda-lime when no copper spiral was used, which proves that small quantities of one or more of the oxides of nitrogen were formed and absorbed by these reagents. The nitrogen determinations of combustion 1 were lost. There is, however, no reason to suppose they would have differed materially from those

¹ Zincke and Kegel: *Ber. d. chem. Ges.*, 23, 246.

² 0.90 cc., equivalent to 0.0011 gram NO from about 0.1 gram picric acid. *Ber. d. chem. Ges.*, 22, 3069.

³ Allowing for nitrogen in reagents. In this table the columns headed "Difference" give the differences between 17.40 and the numbers in the columns immediately preceding.

of 2, which showed no nitrogen was present. In combustion 4, the substance was introduced while the tube was quite warm. Shortly after closing the tube a slight explosion took place. As the stoppers were not blown out, the combustion was completed. The explosion probably accounts for the larger amount of nitrogen found in this case. In 6 and 7, the same soda-lime was used for both. The amount of nitrogen obtained from it, therefore, resulted from two combustions.

To show whether or not these amounts of nitrogen account approximately for the high percentages of carbon and hydrogen when no copper spiral was used, these percentages have been recalculated in combustions 3, 4, and 5, on the hypothesis that the nitrogen was absorbed as nitrogen peroxide, NO_2 . As will be observed, making this allowance causes the results to agree substantially with those when a copper spiral was used.

RECALCULATION OF PERCENTAGES OF CARBON AND HYDROGEN IN
PICRIC ACID.

Combustion number.	NO_2 corresponding to N found in H_2SO_4 . Gram.	Corrected hydrogen. Per cent.	NO_2 corresponding to N found in soda- lime. Gram.	Corrected carbon. Per cent.
3	0.0020	1.60	0.0013	31.65
4	0.0040	1.57	0.0023	31.63
5	0.0006	1.51	0.0018	31.57

The effect of burning picric acid, using a copper boat, was tried with the hope that it would completely reduce any oxides of nitrogen. In some instances the picric acid was also mixed with powdered copper oxide. In every case, however, an explosion of considerable violence occurred, no matter how gradually the tube was heated, so that no results could be obtained.

To show that the Kjeldahl method is accurate for determining small amounts of nitrogen existing in the nitro condition, the results obtained from analyzing very small quantities of dinitrobenzene are given.

NITROGEN DETERMINATIONS WITH DINITROBENZENE.

Amount used. Gram.	Hydro- acid used.	Ammonia to chloric neutralize. N in reagents.	allowing for Titration obtained.	Differ- ence.	Correspond- ing nitrogen.	Theoretical nitrogen in substance taken. Gram.
0.0100	3.00	17.40	16.05	1.35	0.00162	0.00167
0.0100	3.00	17.40	15.92	1.48	0.00177	0.00167
0.0050	3.00	17.40	16.80	0.60	0.00072	0.00083
0.0050	3.00	17.40	16.65	0.75	0.00090	0.00083

This shows conclusively that this method is well adapted to the purpose for which it has been used in this work.

The results of this investigation may be summed up as follows :

Amido compounds, of which urea, hippuric acid, and paratoluidine were taken as types, yield no oxides of nitrogen absorbed by concentrated sulphuric acid or by soda-lime. It is, therefore, not necessary to use a copper spiral when burning them.

Of the nitro substances burned, nitraniline, dinitrobenzene, and picric acid, only the last gave oxides absorbed by the reagents. Judging from the increase in weight of the absorbing tubes, the nitrogen was probably for the most part absorbed as nitrogen peroxide.

Nitric oxide may have been produced to a limited extent in any of the combustions. For, unless this oxide is further oxidized, it is not absorbed by either concentrated sulphuric acid or soda-lime, and consequently has no effect on the accuracy of the determination of carbon and hydrogen.

ADELBERT COLLEGE, CLEVELAND, O.

PARAFFIN AS AN ADULTERANT OF OLEOMARGARINE.¹

BY JOSEPH F. GEISLER.

Received March 23, 1899.

ONE often hears of adulterated food, but rarely are such sophistications of a nature that they may be deemed injurious to health. The recent finding of paraffin as an adulterant in a number of samples of commercial oleomargarine may therefore prove of interest.

Though paraffin has been mentioned as an adulterant of chocolates and candies², the use of such an indigestible substance as an adulterant of oleomargarine seemed so improbable that the actual separation of the paraffin was required to convince some skeptical minds.

Its use in oleomargarine is by no means new, for I first observed it in a commercial sample in September, 1893, and reported the fact to the New York State Department of Agriculture. The general properties of the fat of the sample, its

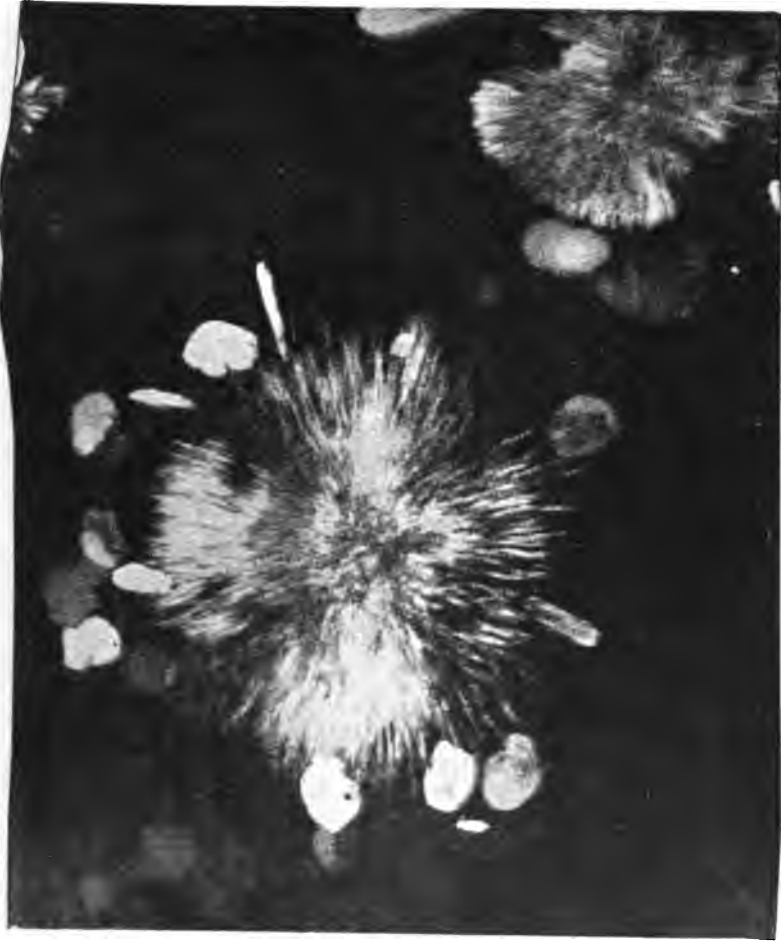
¹ Read at the March meeting of the New York Section.

² U. S. Dispensatory, p. 1091.

behavior during saponification, and the abnormally low specific gravity 0.894 (at $\frac{100^{\circ} \text{ F.}}{\text{water } 100^{\circ} \text{ F.}}$) indicated an irregularity and the probable presence of paraffin. Although the sample under examination amounted to only a few grams, sufficient of the unsaponifiable matter was obtained from the same to show that it was paraffin. It was impossible at the time to get more of this particular sample nor duplicates of several others in which paraffin was found between that date and March, 1894, when I was enabled to prepare an exhibit of the paraffin extracted from one of the samples. About this time experts of the Department of Agriculture, in the course of their inspections in New York and Brooklyn, found quite a number of samples of oleomargarine which, upon analysis, were found to contain paraffin. Some of these were analyzed by Drs. Love, Waller, Stillwell, and myself, and the amounts of paraffin in the various samples were found to range from 9.72 per cent. to 11.25 per cent.

The publicity given the matter at that time possibly caused a discontinuance of the use of paraffin in excessive quantities. At least I did not again observe any positive indications of paraffin in the customary analyses of any of the numerous samples examined until about six months ago and subsequently, when I found paraffin in five different samples which had been taken by the experts of the department in their regular inspections of grocery stores, restaurants, etc., in New York and Brooklyn. One of the samples, a one-pound print, and which had been sold for butter at twenty-two cents per pound, enabled me to make three exhibits of the extracted paraffin. The amounts of paraffin found in these samples ranged from 5 to 11.76 per cent.; in other words, from three to a little over six pounds per sixty-pound tub. The strip of paraffin extracted from commercial oleomargarine which I exhibit herewith, amounting to forty-three grains, is a little short of the amount actually contained in one ounce of one of these samples.

The extent of this character of adulteration it is almost impossible to determine, since much of the goods are sold secretly and in many instances palmed off for butter to unsuspecting purchasers and consumers. That much of the "oleo" in this market is sold under the guise of butter is evidenced by the tes-



Photomicrograph $\times 100$ diameters.

PLATE I.—ADULTERATED OLEOMARGARINE.

Exhibiting appearance of crystallized fat of commercial oleomargarine under microscope and polarized light with crossed Nicols. The white irregular masses are attributable to the presence of paraffin in the sample.

timony of witnesses under oath in hundreds of cases prosecuted in the courts of this city during the past few years. The samples which the inspectors take represent only a small percentage of what goes into consumption. Finally, the samples in the hands of the chemist are, as a rule, not examined with a view of determining possible adulterants, but simply to ascertain whether the substance is butter or a butter substitute. In such examination two to three per cent. of paraffin would scarcely attract the attention of the analyst, while in exceptional cases even five per cent. might go unnoticed, as that quantity will dissolve clear in the alcoholic soap solution under the conditions of the Reichert method for butter analysis. Analysts who are not in the habit of taking the specific gravity of the fat, would in such instances be almost certain to overlook the adulterant.

The samples which would not saponify clear and which gave rise to suspicions on account of the abnormally low specific gravity of the fat, 0.9018 down to 0.8907 at 100° F. (water 100° F.) were the only ones specially examined for paraffin. The fat of one of these samples would not melt clear under 106°, and congealed at 105° F. The separated and purified paraffin from the same had a melting-point of 127°+. The photomicrographs shown herewith were prepared from the fat of this sample. The amorphous masses seen about the fat crystal are due to the presence of paraffin, and were particularly conspicuous in all the slides prepared from this sample. Plate 1 shows the microscopical appearance under polarized light with dark field (crossed Nicols), while in Plate 2 the field is illuminated, producing practically the reverse effect observed in Plate 1. Photomicrograph $\times 100$ diam. The proportions of the Reichert method (two and five-tenths grams of fat to twenty cc. eighty per cent. alcohol containing one gram potassium hydroxide) may be used to advantage in testing for paraffin. The flask with a Liebig condenser attached should be shaken vigorously during the saponification, as this hastens and facilitates the same. After complete saponification, dilute the alcoholic soap solution with an equal volume of water. If two to three per cent. or over of paraffin is present, the solution will turn turbid and much of the separated paraffin can be collected by careful alternate heating and chilling the solution. Such separated matter must of course be examined

as to its identity. A soap solution remaining clear under the above conditions and dilutions would indicate that the fat was free from paraffin, or that it contains under three per cent.

It is pertinent to say that the object of the use of paraffin in oleomargarine is not to cheapen the article, but to make a more homogeneous fat mixture by preventing the separation of the fats and oils, and also to affect the general consistency and appearance of the mass and its behavior under the trier in sampling. One of these samples was with difficulty distinguished from butter by physical tests.

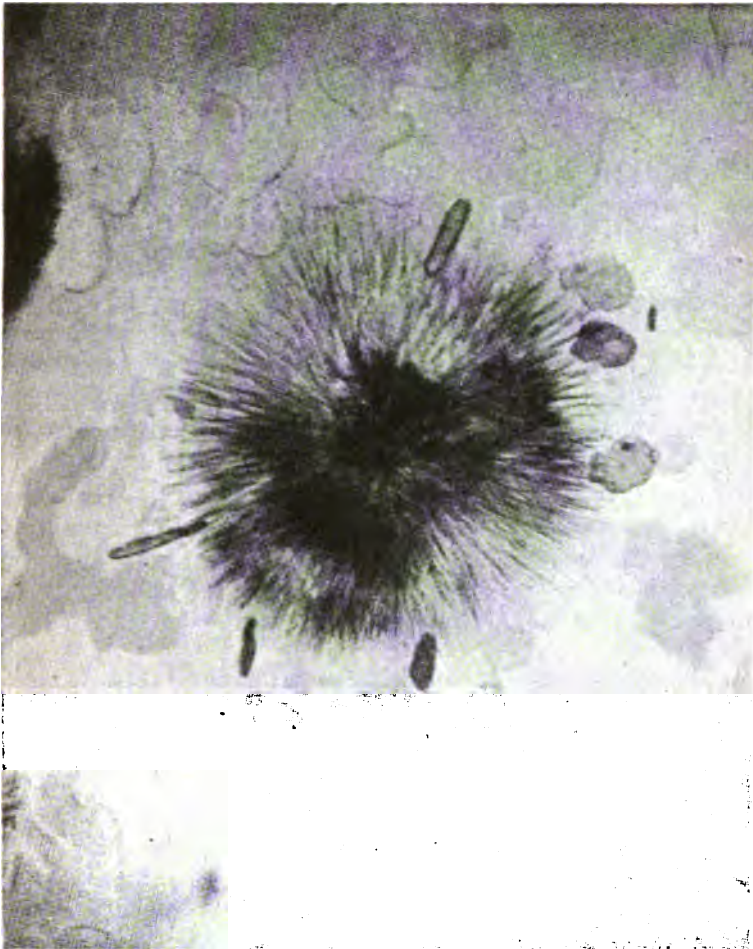
The use of paraffin under these conditions naturally gives rise to the query, What effect has it upon the system? I have been unable to find any records of researches as to the physiological effects of paraffins¹ which throw much light on the subject. Paraffin is generally regarded as an indigestible substance. This is undoubtedly true of paraffin taken into the system by itself. An interesting physiological question, however, presents itself in connection with the use of this substance in oleomargarine for the following reasons:

1. The paraffin is dissolved in the vegetable and animal fats constituting the oleaginous part of the compound.
2. The fat mixture in most cases melts at the normal temperature of the body.
3. The fat mixture is in a highly emulsified condition.

These conditions are so different from those presented in the occasional swallowing of small masses of paraffin that no analogies as to absorbability are presented from which to draw a fair inference. Hager¹ cautions against the internal use of paraffins. It would appear, however, that the symptoms there noted were caused by the lighter petroleums which at that time were commonly called paraffin, and thereby possibly misleading the translators. At the present time there are no data to warrant anyone in saying that the use of paraffin, as above, is harmless in its effects upon the system.

Although paraffin is an unsaponifiable substance, it is a question whether, under the above conditions, some of the paraffin is not absorbed in the system along with the other fats, and whether more serious disturbances may not arise than could be expected from the ordinary digestive disturbances attributable to the indigestibility of the greater part of the adulterant.

¹ Hager: *Pharm. Praxis*, Suppl., pp. 896, 899; *J. Pharm. Assoc.*, 34, 309.



Photomicrograph $\times 100$ diameters.

PLATE II.—ADULTERATED OLEOMARGARINE.

Same crystal as Plate I, but differently illuminated by polarized light and selenite and showing more conspicuously the amorphous masses of irregular shapes.

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XANTHINE BASES IN SUGAR-CANE.

BY EDMUND C. SHORRY.

Received April 3, 1899.

IF a sample of cane-juice be clarified in the ordinary way with lead subacetate, the excess of lead removed by sodium carbonate, or hydrogen sulphide, the solution made alkaline with sodium hydroxide, if not already so, a few drops of Fehling's solution added, and heated to boiling, a whitish precipitate is formed which rapidly becomes green. This was thought to indicate the presence of xanthine bodies. When solutions containing xanthine bases and reducing bodies are treated in this way with Fehling's solution, cuprous oxide is first formed by the action of the reducing bodies, and with this cuprous oxide the xanthine bases unite forming a greenish-white precipitate, Cu, combining with one molecule of the xanthine body. If the Fehling's solution be in excess, and there be also an excess of reducing bodies present, there is of course an excess of cuprous oxide formed, the red color of which hides that of the xanthine compound.

In order to isolate the suspected xanthine base, about ten liters of cane-juice were treated in the way outlined above, enough Fehling's solution being added to give a decidedly red precipitate, the solution filtered, the precipitate well washed, and dissolved in dilute nitric acid. To this solution ammoniacal silver nitrate was added, when a dirty brown precipitate was thrown down.

This silver nitrate precipitate was found to dissolve in nitric acid (sp. gr. 1.10) somewhat slowly on boiling, and the solution so obtained deposited crystals slowly. This indicated the presence of guanine and possibly also of xanthine. A portion of the silver nitrate precipitate was treated with dilute hydrochloric acid, filtered from silver chloride, and the solution evaporated, when crystals were formed having the characteristic microscopic appearance of guanine hydrochloride. The crystals were all of one form, and none of the characteristic crystals of xanthine hydrochloride were observed, proving that no other xanthine body than guanine was present in any quantity.

The guanine hydrochloride so obtained, when treated in water solution, with an excess of ammonia yielded a flocculent white precipitate of guanine, insoluble in water, alcohol, ether, and hot dilute ammonia. This guanine was further identified by Strecker's test: evaporation to dryness with nitric acid and treatment of the residue with caustic potash, when on heating a yellowish red coloration is obtained; also by its conversion into xanthine by nitrous acid:



and the formation of the characteristic crystals of xanthine hydrochloride on treatment with hydrochloric acid.

This isolation and identification of guanine has been repeated on ten samples of juice from mature cane, and on four samples of refuse molasses, and in each case there has been no indication of the presence of any other xanthine body than guanine. It is reasonable then to conclude that in mature sugar-cane guanine is the predominant and probably the only xanthine body present.

During the present season an attempt has been made to estimate the amount of guanine in cane-juice, operating in the following manner: The juice was clarified with lead subacetate, the excess of lead removed by sodium carbonate, and to the filtrate from lead carbonate, heated to boiling, enough Fehling's solution was added to give a decidedly red precipitate; the solution was filtered, and the precipitate well washed with hot water, and the nitrogen contained therein determined and calculated to guanine. One hundred grams of juice were used for each determination and the nitrogen determined by the Gunning method. An average of six samples of juice of approximately the same purity and composition gave

	Per cent.
Total nitrogen.....	0.0350
Guanine nitrogen.....	0.0012
Equivalent to guanine.....	0.0025

From the known properties of guanine, it was thought that this body would go through the processes of sugar manufacture unchanged, but that inasmuch as some of the other nitrogenous bodies are removed during manufacture, the ratio of guanine nitrogen to total nitrogen would be higher in the refuse molasses

than in the original juice. This conjecture was confirmed by guanine determinations in molasses. The average of four samples of refuse molasses of similar composition gave

	Per cent.
Total nitrogen.....	0.7140
Guanine nitrogen.....	0.0308
Equivalent to guanine.....	0.0660

In the samples of raw juice examined the ratio of total nitrogen to guanine nitrogen is 100 : 3.42, while in the refuse molasses the ratio is 100 : 4.31.

The small amount of guanine present in cane-juice is of little technical importance. The amount present in refuse molasses may however be worthy of note in considering the fertilizing or feeding value of the same.

In the analysis of sugar-cane and its products the presence of guanine may introduce an error in some cases unless its presence be recognized. Three of these cases it may be well to note :

1. In the estimation of reducing sugars in technical work the volumetric method with Fehling's solution is generally used; but sometimes when greater accuracy is wished the gravimetric method is used. Now we have already noted that xanthine bodies if present unite with the cuprous oxide formed, and while in the volumetric method this fact introduces no error—for the amount of copper precipitated is not affected—in the gravimetric method by which the cuprous oxide is reduced in a stream of hydrogen, the error introduced is proportional to the amount of guanine or other xanthine base present. The guanine is not affected by the reducing process, and is weighed as copper. It is recommended then that when a gravimetric estimation of reducing sugars is to be made in low grade sugar-house products the electrolytic estimation of the copper be resorted to.

2. A solution of sodium phosphotungstate in sulphuric acid is commonly used as a precipitant of nitrogenous bodies. Guanine in solution is partially precipitated by this reagent not as a compound of phosphotungstic acid but with the sulphuric acid, this compound being sparingly soluble. This may lead to the nitrogen of guanine being credited to other bodies; *e. g.*, peptones. A preliminary treatment with sulphuric acid and filtering before addition of sodium phosphotungstate will remove this source of error.

3. When cane-juice has been clarified with lead subacetate and mercuric nitrate added to the clear solution, a white precipitate is thrown down. This precipitate contains any amide bodies present and by some chemists this use of mercuric nitrate has been proposed or used as a proof of the presence of amide bodies. This is altogether unwarranted, for the mercuric nitrate precipitate contains any guanine present, so that the formation of a precipitate in this case is not only no indication of the amount of amide present, but no evidence of their presence at all.

KOHALA, HAWAII,
March 15, 1899.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE AGRICULTURAL EXPERIMENT STATION.]

A CONTRIBUTION TO THE CHEMISTRY OF BUTTER-FAT.¹

By C. A. BROWNE, JR.

Received April 17, 1899.

THE results on the chemistry of butter-fat herewith presented constitute partly the work on regular experiments at the Pennsylvania Experiment Station, and partly extra work performed at odd moments as the other duties of the laboratory permitted.

Nearly all of the analyses were on samples of butter made at the Station Creamery, and representing for the most part the product of a herd of high-grade Guernseys. The figures given in the tables, accompanying this article, need not be taken, therefore, as typical of butter-fats in general, though we believe them to be, on the whole, fairly representative. The differences, if there are any, in the chemical composition of butter-fat from different breeds of cows, is a subject at present being investigated at this station.

We have chosen, for the sake of convenience, to divide our subject into three distinct heads; *viz.*,

1. The physical and chemical constants of butter-fat.
2. The chemical composition of butter-fat.
3. The chemistry of rancidity in butter-fat.

Each of these divisions will constitute a separate paper.

¹ Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

I. THE PHYSICAL AND CHEMICAL CONSTANTS OF BUTTER-FAT.

A word should be said in regard to the preparation of samples of butter-fat for analysis. The method of procedure adopted in this laboratory is as follows: A sufficient quantity of the butter is placed in a glass jar or beaker and warmed at about 50° C., with occasional agitation, until the water and curd have separated out, leaving the layer of butter-fat quite clear. Then, without disturbing any of the water and curd, as much as possible of the melted fat is drawn off with a pipette into another vessel and allowed to stand, if necessary, for further clarification. The sample is then filtered through desiccated filter-paper into a clean, dry jar, after which it is stoppered and preserved for analysis in a cold place away from the light. The special precaution to be noted, in the preparation of the samples, is the avoidance of too high a temperature in melting. Butter-fat is an exceedingly unstable body and a temperature much above 50° C. will very soon produce chemical changes. Too long an exposure at 50° C. even, will alter the composition of butter-fat,¹ so that no more time than is necessary should be consumed in the processes of melting and filtering.

In Table I are given the results obtained for a few of the common constants usually determined in butter-fat analysis.

TABLE I.²

Constant.	Range.	Mean.	Number of samples represented.
Specific gravity $\frac{40^{\circ}}{30}$	0.9050-0.9102	0.9073	35
Melting-point.....	31.6°-34.6°	33.2°	35
Acid number.....	0.20-0.66	0.50	5
Saponification number.....	224.0-234.9	228.5	40
Ether number ³	223.5-234.4	228	40
Iodine number.....	29.36-37.30	33.35	40
Reichert number (two and a half grams).....	15.10-17.50	16.2	40
Reichert-Meißl number (five grams)	22.80-32.10	28.3	10
Insoluble acids, per cent	86.03-88.84	87.65	10

¹ We have found by experiment that a butter-fat kept at 50° C. for two days suffered a decrease in its iodine number of over one unit.

² The figures from which this and succeeding tables are made up represent the mean of duplicate determinations.

³ Saponification number less 0.5, the mean acid number.

The constants were all determined by the usual processes employed in the analysis of oils and fats; since these are too well known to require any detailed description, we will simply indicate the methods employed, describing only any modifications which were introduced.

The specific gravity was determined on the melted samples at 40° C. by means of a Westphal balance, which gives results accurate to the fourth decimal. Whenever greater accuracy was required a pycnometer or Sprengel tube was used.

The melting-point was determined according to the method of the official chemists.¹

The acid number, or milligrams of potassium hydroxide necessary to neutralize the free acid in one gram of fat, was determined by heating about ten grams of the fat with fifty cc. of neutral alcohol in a ten-ounce flask provided with a condensing tube. After allowing the alcohol to boil for several minutes, the flask was cooled to about 50° C., when the condensing tube was removed, and the contents titrated with tenth-normal alkali (sodium hydroxide or potassium hydroxide), using phenolphthalein as indicator.

The determinations of the acid number were made upon samples of fat taken immediately after the butter was churned, so it will be observed that, even when fresh, butter-fat contains an appreciable amount of free acid. This is a fact of some importance upon which we will dwell more fully when treating of the subject of rancidity.

The saponification number, or milligrams of potassium hydroxide necessary to saponify one gram of fat, was determined according to the usual method. About two and a half grams of fat were taken and saponified with exactly twenty-five cc. of half-normal alcoholic potassium hydroxide. To secure concordant results great care must be exercised in regard to the measuring of the potassium hydroxide solution; for this reason we prefer a burette to the twenty-five cc. pipette generally recommended. The saponifications were performed in flasks provided with condensing tubes; twenty to thirty minutes were usually allowed for the reaction, after which the contents of the flask were titrated back with half-normal hydrochloric acid, using phenolphthal-

¹ Bulletin No. 46, Division of Chemistry, U. S. Department of Agriculture, p. 34.

ein as indicator. Blank experiments were run with every series of determinations.

The ether number, or milligrams of potassium hydroxide necessary to saponify the neutral fat in one gram of sample, is found by subtracting the acid number from the saponification number.

The iodine number, or percentage of iodine absorbed by the fat, was determined according to the method of the official chemists.¹ A burette was used for measuring the iodine solution as more concordant results could be secured than when a pipette was employed.

The volatile acid numbers were determined partly by the Reichert method, when two and a half grams of fat were taken, and partly by the Reichert-Meissl process, when five grams of fat were employed. With the exception of the quantity of fat weighed out the method of procedure was the same in both cases, Wollny's process² for saponification and distillation being the one adopted.

It is a well-known fact that the method of determining the volatile acids in butter-fat by the ordinary process of distillation is not a quantitative one. The number of cubic centimeters of half-normal alkali consumed is always greater by the Reichert process, as a larger percentage of the volatile acids are driven over when working with a smaller quantity of fat; the results in Table I show that the Reichert process gives a mean constant ten per cent. higher than the Reichert-Meissl method, after calculating the figures both to the same weight of fat.

Richard Meyer found that by distilling with a current of steam, the number of cubic centimeters of half-normal alkali was increased by twenty-five per cent. The experience in this laboratory has been that only from seventy-five to eighty per cent. of all the volatile acids pass over in one distillation. As a test, ten distillations were made on two and a half grams of fat, the contents of the flask being replaced with 110 cc. of water after each distillation. The first fraction took 15.5 cc. of tenth-normal alkali, the succeeding nine fractions requiring each in their order, 2.00, 0.95, 0.60, 0.55, 0.40, 0.35, 0.30, 0.30, 0.25, or

¹ Bulletin No. 46, Division of Chemistry, U. S. Department of Agriculture, p. 32.

² *Ztschr. anal. Chem.* (1889), 28, 721.

together 5.7 cc., giving a total of 21.2 cc., thus making the original Reichert number of 15.5 over twenty-five per cent. too small.

Instead of distilling the lower fatty acids it is possible to remove them from the higher insoluble acids by washing.¹ The process can be carried out in connection with the determination of the saponification number, or with the determination of the insoluble acids. If worked in connection with the former the method of procedure is as follows :

Having determined the saponification number of the fat the flask is replaced on the steam-bath until all alcohol is removed. The residue of soap is then dissolved in 100 cc. of hot distilled water, and after cooling to about 60° just enough half-normal hydrochloric acid is added to unite with all the combined alkali.² The flask is then stoppered with a condensing tube and heated on the steam-bath until the fatty acids have risen to the surface and the liquid underneath has become clear. The flask and contents are now thoroughly cooled, after which the cake of insoluble fatty acids is gently detached from the walls of the flask by shaking and the liquid filtered into a liter flask. One hundred cc. of hot water are then poured into the flask and, after the acids have melted, thoroughly shaken. The contents of the flask are poured on the filter and the flask again washed out with hot water; this is repeated until all the fatty acids are removed from the flask, when they are washed directly on the filter. As soon as the filtrate amounts to a liter it is titrated with half-normal alkali. It is needless to remark that the water used for washing should be absolutely neutral.

Although a larger percentage of the lower acids are generally removed by the above process of washing than by one distillation, the same difficulty of effecting a complete separation of the soluble from the insoluble acids is experienced. It has been found impossible to remove the last traces of soluble acids, even by continued washings, the higher and less soluble homologues, caprylic and capric acids, especially being retained by the insol-

¹ Allen: Commercial Organic Analysis (1899), Vol. II, Part 1, p. 191.

² The amount of half-normal hydrochloric acid necessary for this can be found by subtracting the number of cubic centimeters of half-normal hydrochloric acid used in titrating the excess of potassium hydroxide in the determination of the saponification number from the number of cubic centimeters of half-normal hydrochloric acid used to neutralize the potassium hydroxide in the blank experiment.

uble acids on the filter. The first filtrate (one liter) of soluble acids from a butter-fat, treated by the process of washing just described, required 15.5 cc. of tenth-normal alkali. The acids on the filter were washed nine more times, using a liter of hot distilled water at each washing. The succeeding filtrates required each in their order, 1.05 cc., 0.60, 0.50, 0.40, 0.35, 0.35, 0.30, 0.30, 0.15, making in all 19.5 cc. It is evident that, while one treatment is amply sufficient to distinguish a butter from a substitute, the method is of little value quantitatively unless the treatment of washing be repeated until the washings become neutral—a tedious operation at the best.

The process employed by us for determining the percentage of insoluble acids, or Hehner number, is as follows: Ten grams of the fat are weighed out into a wide-necked 250 cc. flask and saponified with five cc. of fifty per cent. soda and twenty-five cc. of ninety-five per cent. alcohol. The alcohol is then distilled off and the residue of soap dissolved in 150 cc. of water; 50 cc. of hydrochloric acid (1 : 1) are then slowly added with continuous shaking, after which the flask is replaced on the steam-bath and allowed to stand until the liquid beneath the layer of fatty acids has become perfectly clear. The flask and contents are now cooled; the cake of fatty acids, after hardening perfectly, is loosened from the walls of the flask by shaking gently, and the liquid underneath poured through a clean filter. The short arm of a glass siphon is then introduced, allowing the end of the tube to come in contact with the bottom of the flask; the discharging end of the siphon is closed by a piece of gum tubing fitted with a pinch-cock. The flask is now filled about three-fourths full with hot water and thoroughly agitated; after allowing the fatty acids to rise to the surface of the liquid, the siphon is filled by blowing in hot water from a wash-bottle at the lower end, the process being easily controlled by the pinch-cock. In this way also any of the fatty acids, which have risen within the siphon, can be washed back into the flask. The liquid underneath the layer of fatty acids is now siphoned off into the paper used for the first filtration, the pinch-cock serving to regulate the flow. When as much as possible of the liquid is drawn off, without taking any of the insoluble acids, the flask is again nearly filled with hot water and shaken; after washing out the siphon, the

liquid is drawn off as before. The process is continued until the washings cease to redden litmus paper; about ten washings, requiring over two liters of water, are generally necessary to effect this. When the washings are neutral the siphon is removed, any acids, which may remain adhering to it, being washed back into the flask with hot water; the flask is cooled and as soon as the acids have hardened the cake is detached and the washings poured through the filter. The flask is then placed in an inverted position over the filter and allowed to drain over night. In the morning the filter-paper, which generally contains a small quantity of insoluble acids, is washed several times with a few cubic centimeters of ether, the washings being allowed to run into the flask. The flask is then warmed at 80° until most of the ether is expelled and then dried at 100° to constant weight. We have found it expedient to dissolve out the acids, after securing a constant weight, with hot alcohol and reweigh the flask; a difference of several milligrams is generally experienced between the first and last weighings, due to the removal of soluble matter from the glass.

We believe a quicker and more thorough washing of the insoluble acids, with less danger of loss, is secured by this method than by the usual processes for determining the insoluble acids. Duplicate results can be secured which agree perfectly. The method is applicable not only to the analysis of fats and oils, but we have used it to advantage in soap analysis.

One point which we have observed in connection with the drying of fatty acids to constant weight at 100° C. is that when the acids were dried in a low evaporating dish or beaker a constant weight could never be secured; the acids continued to lose in weight even when it was evident that all moisture was removed; when, on the other hand, the drying was performed in a flask a constant weight was soon secured, after which no change was observed, even on many hours' drying. This difference we believe to be due to a partial volatilization of the insoluble acids; the escape of volatile products would be much easier from an open dish than from a flask; moreover, we have always found, after removing the flask containing the insoluble acids from the oven, that the inner surface and lower parts of the neck of the

flask were coated with a thin layer of condensed acids, showing that a volatilization must have occurred.

In Table II are given figures for a few of the constants less frequently determined in the analysis of butter-fat.

TABLE II.

Constant	Range.	Mean.	Number of samples represented.
Acetyl number.....	3.5-4.8	4.1	5
Glycerol calculated ¹	12.24-12.79	12.46	40
" by analysis.....	12.30-12.70	12.45	10
Total fat acids calculated ¹	94.72-94.94	94.85	40
Soluble fat acids calculated ...	6.52-8.96	7.20	10
Specific gravity $\frac{1}{100}$ insoluble acids	0.9106-0.9242	0.9162	10
Melting-point insoluble acids	40.2°-42.7°	41.7°	10
Saponification number insoluble acids.....	212.5-217.0	214.5	10
Mean molecular weight insoluble acids.....	258.1-263.5	261.0	10
Specific gravity $\frac{1}{100}$ soluble acids	0.9475-0.9483	0.9479	2
Saponification number soluble acids	563.7-577.3	571.7	15
Mean molecular weight soluble acids.....	97.17-99.52	98.12	15

The acetyl number, or milligrams of potassium hydroxide necessary to combine with the acetic anhydride in one gram of acetylated fatty acids, was determined according to the method of Benedikt and Ulzer.² The process, as conducted in this laboratory, is as follows:

Fifty cc. of the melted fat are saponified, the resulting soap is decomposed with hydrochloric acid, and the insoluble acids secured according to the usual methods. Twenty-five cc. of the dried and filtered acids are boiled with twenty-five cc. of glacial acetic acid, for two hours, in a 250 cc. flask connected with a reflux condenser. The mixture is then poured into a large two-liter flask filled three-fourths full with boiling water; the flask is thoroughly agitated for some minutes and then allowed to stand until the acids have risen to the surface. After cooling perfectly under running water, the cake of acids is gently

¹ Calculated from figures given for ether numbers in Table I.

² *Monatsh. Chem.*, 8, 40; *Analyse der Fette*, 3rd Ed., p. 146.

detached from the walls of the flask and the liquid underneath poured out; the flask is then filled half full with hot water and the contents boiled for half an hour; a few pieces of clean pumice stone, which have been kept under water, are added to prevent bumping. The liquid underneath the acids is then removed by a siphon and the acids washed by siphonation, as under determination of insoluble acids, until the wash-water is neutral. The acids in the flask, after hardening, are allowed to drain; they are then melted, transferred to a smaller vessel, and dried at 100° until all water is removed, after which the acids are filtered through dry paper and preserved for analysis.

To determine the acetyl number, three to five grams of the acetylated acids are weighed out into a 250 cc. flask, dissolved in fifty cc. of neutral alcohol, and titrated with half-normal alcoholic potash, using phenolphthalein. The milligrams of potassium hydroxide for one gram of acid are calculated as in the determination of the acid number, and the number so obtained is designated the acetyl-acid number. An excess of the alcoholic potassium hydroxide is then added, the flask is stoppered with a condensing tube, and heated on the bath twenty to thirty minutes, after which the excess of potassium hydroxide is titrated back with half-normal hydrochloric acid. The quantity of potassium hydroxide consumed by this second process, when expressed in milligrams per gram of fat, constitutes the acetyl number. The sum of the acetyl-acid number and acetyl number is known as the acetyl-saponification number. The acetyl number then represents simply the ether number of the acetylated acid, being the difference between the acetyl-acid and acetyl-saponification numbers.

In reviewing the literature of the subject only two other values could be found for the acetyl number of butter-fat. Wachtel gives 9.6, and Bondzynski and Ruff 18.2, numbers both considerably higher than the values given in Table II. The acetyl figure, though of little value in practical butter analysis, yet furnishes us a measure of the oxy-acids in a fat; more will be said as to the employment of this constant under the subject of rancidity.

The percentage of glycerol which a butter-fat will yield upon saponification can be readily calculated from the ether number.

In the saponification of any triglycerid three molecules of potassium hydroxide separate one molecule of glycerol, or 168.3 parts of potassium hydroxide corresponds to ninety-two parts of glycerol; one gram, therefore, of potassium hydroxide would equal 0.5466 gram of glycerol.¹ If E represents the ether number of a fat, the percentage of glycerol, G, which the fat will yield, will be,

$$G = 0.05466 E.$$

This indirect method of estimating glycerol can be used in the analysis of any fat or oil which belongs to the class of triglycerids: with diglycerids the method is not practicable as Benedikt has shown.² With rancid fats, owing to the presence of aldehyde bodies, as will be shown later, the method gives too high results.

The percentage of glycerol was determined directly by the method of Benedikt and Zsigmondy,³ which is based upon the fact that one molecule of glycerol, when oxidized in a strongly alkaline solution with permanganate, produces quantitatively exactly one molecule each of oxalic acid and carbon dioxide.



Allen's⁴ modification of the original process of Benedikt and Zsigmondy, was followed in this laboratory with the exception of a few minor differences.

Ten grams of butter-fat are weighed out into a six-ounce saponification flask of heavy glass provided with a tightly fitting glass-stopper. Five grams of potassium hydroxide dissolved in fifty cc. of water are then added and the glass stopper wired in securely. The flask is placed in the steam-bath and shaken thoroughly every fifteen minutes, the heating being continued until the contents of the flask become thick and homogeneous, and no more liquid fat is seen swimming on the surface: eight to twelve hours is generally necessary for this. When saponification is complete the flask is cooled, unstoppered, and the contents washed out into a large beaker with 200-300 cc. of hot water. A perfectly clean solution should be obtained without any oily particles being visible.

¹ Zulkowski: *Ber. d. chem. Ges.*, 18, 1140.

² Benedikt: *Analyse der Fette und Wachsarten*, 3rd Ed., p. 182.

³ *Ibid.*, p. 182.

⁴ *Chem. Ztg.*, 9, 975. *Analyse der Fette*, p. 182.

⁵ Allen: *Commercial Organic Analysis*, 3rd Ed., (1899), Vol. II, Pt. 1, p. 314.

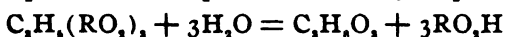
The solution of soap is decomposed with an excess of dilute sulphuric acid, and the fatty acids separated and washed in the usual way; the washings, which should be clear, are made up to one liter and thoroughly mixed. 200 cc. (two grams of fat) of this solution are measured out into a large evaporating dish or beaker, diluted to about 400 cc. and neutralized with potassium hydroxide solution using phenolphthalein. Ten grams of solid potassium hydroxide are then added, and when completely dissolved, a saturated solution of permanganate is added, at ordinary temperature, until the liquid is colored no longer green, but a very dark-blue (three to five grams of permanganate are sufficient for this). The solution is then heated to gentle boiling for about an hour, the liquid becoming finally red with precipitation of the hydrated peroxide of manganese; the volume of the liquid, during the boiling, should be kept at about 400 cc. by adding water from time to time. A strong solution of sodium sulphite is then gradually added until all color is destroyed, and the liquid above the brown precipitate is clear. The solution is next filtered through a large funnel, using heavy filter-paper, into a liter flask, and the precipitate washed with hot water until the flask is nearly full; the slight turbidity, which frequently shows in the final washings, does no harm. After cooling and making up to one liter, 500 cc. (one gram original fat) are measured into a large beaker, acidified with acetic acid, heated nearly to boiling, and precipitated with ten cc. of a ten per cent. calcium chloride solution; the liquid is heated on the steam-bath an hour or more until everything has settled out. The precipitate, consisting of calcium oxalate, with a little sulphate mixed, is filtered into a prepared Gooch crucible and thoroughly washed with hot water. The contents of the Gooch crucible, including the asbestos felt, are then washed back into the original beaker with about 200 cc. of hot water, acidified with dilute sulphuric acid, and heated on the bath for ten minutes, after which the solution is titrated with tenth-normal permanganate. One cc. of tenth-normal permanganate equals 0.0046 gram of glycerol.

The oxidation method for determining glycerol is a somewhat long and tedious one, requiring also a certain amount of practice to secure good results. The details of the method, as regards

the oxidation, must be rigidly adhered to. Benedikt¹ states that the soluble fatty acids, butyric, etc., which are present in the same solution with the glycerol, do not yield oxalic acid on the treatment with potassium hydroxide and potassium permanganate, but that this is true only so far as regards the original method. Johnstone² and Mangold have both found that in strongly alkaline solutions butyric acid can be oxidized to oxalic acid. Experiments in this laboratory confirm this; if too great an excess of either potassium hydroxide or potassium permanganate is used for oxidation, or if during the process of boiling, the liquid is allowed to become too concentrated, abnormal results are secured. A butter-fat which gave 12.35 per cent. of glycerol, when analyzed according to the method, yielded, according to analysis, over eighteen per cent. of glycerol, by employing a large excess of potassium hydroxide and potassium permanganate, and oxidizing in a concentrated solution, thus proving beyond doubt that the soluble acids had been acted upon. By observing the necessary precautions, however, no danger need be apprehended from this source; we have found the method to yield most excellent results on many of the ordinary fats, as well as on butter-fat itself, the agreement between the percentage of glycerol as calculated from the ether number, and as determined by analysis, being very close, as the following examples will show.

Fat.	Ether number.	Glycerol calculated. Per cent.	Glycerol by analysis. Per cent.
Beef-tallow	195.5	10.68	10.61
Commercial stearin	192.3	10.51	10.56
Butter-fat	232.2	12.69	12.70

The total percentage of fatty acids which a butter-fat will yield can be readily calculated if we know the percentage of glycerol produced on saponification.³ By inspecting the formula,



Fat + water (54) = glycerol (92) + fatty acid,

we observe that in saponifying a fat fifty-four parts of water are required for every ninety-two parts of glycerol produced. The yield of fat acids (*F*) from 100 parts of fat would be represented

¹ *Analyse der Fette*, 3rd Ed., p. 184.

² *Chem. News*, 63, 11.

³ Zulkowski: *Ber. d. chem. Ges.*, 16, 1315.

then by the formula, $F = 100 + \frac{54}{92} G - G$, or $F = 100 - \frac{38}{92} G$, in which G equals percentage of glycerol. G , as we have shown, can be obtained from the ether number (E) of a fat by the formula, $G = 0.05466 E$; by substituting this value for G in the previous equation we obtain, $F = 100 - \frac{38}{92} \times 0.05466 E$ or $F = 100 - 0.02258 E$.¹

The percentage of soluble acids in a butter-fat can be found by subtracting the percentage of insoluble acids (Hegner's number) from the percentage of total acids.²

The specific gravity of the insoluble acids was determined by weighing the acids in air and in water at 20°, using a sinker. For a sinker we have found a small platinum crucible cover to answer very satisfactorily, since it offers a convenient receptacle for holding the acids; a silk thread is used for suspending the cover from the beam of the balance; no air-bubbles should be present on the surface of the sinker during the operation and to prevent their appearance recently boiled distilled water is used throughout the work. The following example will illustrate the method:

Weight of sinker and fatty acids in air = 6.5460 grams			
"	"	" alone	" " = 5.2110 "
"	"	insoluble fatty acids	" " = 1.3350 " = w
"	"	sinker in water at 20°	= 4.9715 " = ω
"	"	" and acids in water at 20°	= 4.8405 " = ω'

From the formula $s = \frac{w}{w + \omega - \omega'}$, we calculate the specific gravity of the insoluble acids to be 0.9106. This formula is sufficiently accurate for ordinary purposes; more strictly it should read, $s = \frac{w(1-s)}{w + \omega - \omega'} + s$, in which s equals the density of air; the value of s for dry air, within the ordinary range of temperature and pressure, is 0.0012. If we desire to express the gravity in terms of water at 4° we should use the formula $s = \frac{w(d-s)}{w + a - \omega'} + s$, where d equals the density of water at the temperature of the

¹ Benedikt: *Analyse der Fette*, 3rd Ed., p. 162.

² *Ibid.*, p. 165.

experiment, a value easily found from tables. At 20° d is 0.9982, our original specific gravity, then, corrected to $\frac{20^{\circ}}{4^{\circ}}$ would be 0.9091 instead of 0.9106.¹

The melting-point of the insoluble acids was determined by observing the temperature at which the acids became transparent when heated in a capillary tube. A small piece of capillary tubing, about one inch in length, is sealed at one end and nearly filled with the melted fatty acids; there should be no air space beneath the fatty acids and to prevent this, the filling of the tube is best accomplished with a small pipette or dropper, the end of which has been drawn out to a slender point. The tubes should be filled and cooled several hours before making the determinations.

In conducting the experiment the small tube containing the fatty acids is fastened to the bulb of a delicate thermometer and then lowered into a large test-tube, nearly full of distilled water recently boiled and cooled; the test-tube is fastened into a tall beaker nearly filled with water. Heat is now gently applied, keeping the water in the outer vessel constantly stirred by means of a blowing bulb. As soon as the temperature of the water in the beaker reaches 38° , the heat is raised more slowly, about 1° in five minutes. A difference of about 1° is generally observed between the beginning of melting and the point of absolute transparency; we have used the latter as the true melting-point, though the mean of the two readings would be perhaps a little more correct. The method of the official chemists would not be practicable in the case of determining the melting-point of the insoluble acids, owing to the solubility of the acids in alcohol.

The saponification number of the insoluble acids, which in this case would be identical with the acid number, was determined by dissolving three to five grams in hot neutral alcohol and titrating with half-normal potassium hydroxide.

From the saponification number (s),² the mean molecular

¹ This method can be used as well for determining the specific gravity of butter-fat at the ordinary temperature. We have found the mean specific gravity of butter-fat corrected to $\frac{20^{\circ}}{4^{\circ}}$ to be 0.9250.

² *Analyse der Fette*, p. 163.

weight (m) of the insoluble acids can be readily calculated by means of the formula $m = \frac{56100}{s}$.¹

For the determination of the constants of the soluble acids from butter-fat, it is necessary first to separate the acids in a state of complete purity. To effect this the following process was employed :

One hundred grams of butter-fat were saponified with fifty cc. of fifty per cent. sodium hydroxide solution and 200 cc. of alcohol in a large flask provided with a condensing tube. After distilling off the alcohol, the residue was dissolved in hot water, decomposed with excess of hydrochloric acid (1 : 1), and heated on the bath using the condensing tube, with occasional shaking until the liquid underneath the layer of acids had become clear. The contents of the flask were then cooled, the cake of acid detached, and the liquid underneath filtered through heavy paper into a large evaporating dish. The insoluble acids were then remelted, brought upon the filter with hot water and washed until the filtrate became neutral. The combined filtrates and washings were neutralized with sodium hydroxide solution using phenolphthalein and evaporated to about 500 cc.; the solution was next filtered into a large separating funnel, acidified with dilute sulphuric acid, and after cooling shaken with fifty cc. of washed ether. After standing for a few minutes, the two solutions were separated and the aqueous liquid again treated with fifty cc. of ether; the process was repeated for a third time when the combined ethereal solutions were filtered into a dry dish and the ether allowed to evaporate at the room temperature; the residue of soluble acids² (five to six grams) was dried in a vacuum over sulphuric acid and then preserved in a stoppered vial. The soluble acids thus obtained consisted of a light mobile liquid having a pale

¹ In the *Chem. Rev. Fett u. Harz-Ind.*, 5, [9], 169-172, R. Henriques calls attention to a difficulty in estimating the mean molecular weight of the insoluble acids from butter-fat, in that the values found on drying the acids at 105°-110°C. (*viz.*, 267-270) differed from those (256.3-263) obtained when the drying was effected at the ordinary temperature in a vacuum. (Abstract in *Analyst*, No. 274, p. 7.)

The values found by Henriques on drying in a vacuum are identical with those given by us in Table II. The higher values, found on drying the acids at 105°-110°, we believe to be due to a partial volatilization of acids of low molecular weight, such as lauric and myristic, which, as will be shown in a later article, are present in the insoluble acids of butter-fat in considerable quantity. Such a volatilization may occur at even 100°, as we have already indicated (p. 618).

² A quantitative separation of the soluble acids is not effected by the treatment.

straw color,¹ and giving the intense odor characteristic of butyric acid.

The specific gravity of the soluble acids was determined at 20° C. by means of a small two cc. pycnometer.

The saponification number was determined by titrating one to two grams of the acids, dissolved in neutral alcohol, with half-normal potassium hydroxide. Knowing the saponification number (*s*) the mean molecular weight of the soluble acids is determined by the formula $m = \frac{56100}{s}$.

We are well aware that the figures given in Table II for the mean molecular weight of the soluble fatty acids are much lower than those given by certain German authorities. Benedikt² gives 139 as the mean molecular weight of the volatile fatty acids from butter-fat. This number was not found directly, however, but was calculated on the assumption that the Reichert-Meissl number is a quantitative expression for the amount of volatile acids, an assumption not warranted by experiment as has been shown.³

If the calculation be made on the volatile acid number from ten distillations instead of from one, results will be obtained which approximate very closely those expressed in Table II, as the following example will show. A butter-fat, containing 8.72 per cent. of soluble acids, required to neutralize the volatile acids (ten distillations) from 2.5 grams, 22.3 cc. of tenth-normal sodium hydroxide, or 8.92 cc. of tenth-normal sodium hydroxide per gram of fat. $\frac{8.72}{8.92} \times 100 = 97.7$, the mean molecu-

lar weight of the soluble acids. Practically the same figure is arrived at, if we obtain the saturation number of the soluble acids, after their complete removal by washing, according to the method already described.⁴ Two and five-tenths grams of a butter-fat, containing seven and seven-tenths per cent. of soluble acids, required 19.5 cc. of tenth-normal sodium hydroxide to neutralize the soluble acids removed by washing. The cubic

¹ If distilled in a vacuum the acids can be obtained colorless.

² *Analyse der Fette*, 3rd ed., p. 546.

³ This article, p. 615. Benedikt, elsewhere in his own work, calls attention to this same fact. *Analyse der Fette*, 3rd ed., p. 137.

⁴ This article, p. 617.

centimeters per gram of fat would be seven and eight-tenths and the mean molecular weight would equal $\frac{7.7}{7.8} \times 100$ or 98.7.

We have determined the mean molecular weight of the volatile acids in many butter-fats by still another process. The weight of the barium salts of the volatile acids, is determined and, from the amount of barium oxide contained therein, the mean molecular weight of the combined acids is calculated by means of the formula $m = \frac{76.7(r-b)}{b} + 9$, in which m is the mean molecular weight sought, r the weight of barium salts, and b the weight of barium oxide. The process can be carried out in connection with the determination of the Reichert or Reichert-Meissl number. After neutralizing the distillate of volatile acids with half-normal barium hydroxide, the solution is evaporated to dryness in a weighed platinum dish, and heated at 100° C. to constant weight. The residue is then moistened with a little strong sulphuric acid, ignited, and weighed; from the weight of barium sulphate is calculated the barium oxide. A comparison of the values obtained for the mean molecular weight of the volatile or soluble acids by the above method and by the method of direct titration is given herewith:

	Range.	Mean.
By direct titration.....	97.94-99.51	98.73
" weighing the barium salts.....	97.17-98.97	97.92

We can verify this figure for the mean molecular weight of the volatile or soluble fatty acids in the following manner:

For the average butter-fat we may consider the following constants to be nearly correct:

Saponification number	228.5 (Table I)
Insoluble acids, per cent	87.65 "
Soluble " "	7.20 (Table II)
Saponification number of insoluble acids..	214.5 "

There are required then for the average butter-fat:

228.5 mg. KOH to saponify 1 gram of fat	
$0.8765 \times 214.5 = 188.0$ " " " "	insoluble acids in 1 gram fat
Difference 40.5 " " " "	soluble acids in 1 gram fat

or 40.5 mgs. of KOH are required to saponify 0.0720 gram of

soluble acids. Therefore $\frac{40.5}{0.072} = 562.5$, theoretical saponifica-

tion number of soluble acids, and $\frac{56100}{562.5} = 99.73$, theoretical molecular weight of the soluble acids in the average butter-fat. While this theoretical figure is a trifle higher than any we have found in actual work, the agreement is sufficiently close to enable us to say that the mean molecular weight of the soluble acids from butter-fat lies very near to the value expressed in Table II.

We have often found it convenient in our work, where an accurate determination was impossible, either from want of time, or lack of material, to make a rough approximation of the percentage of soluble acids; for this purpose we have devised a very simple formula, the only factor necessary to know being the saponification number of the butter-fat. The equation, in which v equals per cent. of soluble acids and s the saponification number, is :

$$v = 0.0018 \left[s - \left(188.5 + \frac{228-s}{2} \right) \right] \times 100, \text{ or } v = 0.09(3s - 605).$$

The formula is deduced from data given in the preceding tables. The average butter-fat, having a saponification number of 228, and containing 87.65 per cent. of insoluble acids with a saponification number of 215, would require 188.5 milligrams of potassium hydroxide to neutralize the insoluble acids from one gram of fat. For any butter-fat, having a saponification number s , this value was found to be about $188.5 + \frac{228-s}{2}$. From the

molecular weight of the volatile or soluble acids, we find that one milligram of potassium hydroxide neutralizes 0.0018 gram of soluble acids; the difference, therefore, between the saponification number of the butter-fat and the milligrams of potassium hydroxide required for the insoluble acids, multiplied by 0.0018, gives the weight of soluble acids per gram of fat; multiplying this by 100 we arrive at the percentage of soluble acids sought.

The formula is not expected to give results absolutely accurate in any case, since variations in the saponification number of a butter-fat are caused to a considerable extent by differences in the molecular weight of the insoluble acids, differences which the formula, as given, does not take into account.

THE RELATION BETWEEN THE CONSTANTS OF DIFFER-
ENT BUTTER-FATS.

It was observed, in tabulating the results from many analyses of butter-fat, that there existed a certain ratio between some of the different constants. An inspection of the following table will illustrate this point.

TABLE III.

Butter-fat.	Saponification number.	Reichert number.	Iodine number.	Melting-point.	Specific gravity. $\frac{40^{\circ}}{15.5^{\circ}} \text{C.}$
1	226.1	15.3	34.85	33.5 ^c	0.9092
2	226.3	15.6	34.58	34.5 ^o	0.9058
3	226.9	15.7	35.45	33.8 ^o	0.9070
4	230.9	16.1	33.67	32.5 ^o	0.9058
5	232.7	16.2	30.96	33.0 ^o	0.9085
6	232.9	16.3	29.56	32.4 ^o	0.9068

We notice that with an increase of the saponification number a quite uniform increase of the Reichert number takes place, while the iodine absorption decreases; these are such variations as one would expect; a higher percentage of oleic acid of low combining power would raise the iodine number and tend to diminish the saponification value; similarly an increase in the percentage of the soluble acids of high combining power would elevate both the Reichert and the saponification numbers.

Table IV comprises a few of a large number of butter-fats analyzed at this station by Mr. W. S. Sweetser in 1894, and illustrates this relation even more pointedly than Table III.

TABLE IV.

Butter-fat.	Saponification number.	Iodine number.	Reichert number.
1	218.8	41.32	17.1
2	222.4	37.30	17.5
3	224.6	37.00	18.6
4	232.5	30.21	19.4
5	236.2	27.17	20.8
6	241.5	25.91	21.3

From these tables it would seem as if the percentages of oleic and of the soluble acids in different butter-fats bore a ratio somewhat complementary to one another. It must be remembered that the relations, which the foregoing tables represent, are only general, and by no means fixed; there are butter-fats which show constants bearing relations different from those expressed

above, and from isolated cases a table might be constructed showing exactly opposite tendencies. As regards specific gravity and melting-point, no definite relation could be discovered, though the latter showed a tendency to diminish as the saponification and Reichert numbers increased.

ABNORMAL BUTTER-FATS.

Different observers have reported from time to time cases in which butter-fats showed chemical and physical constants of such abnormality that, were the samples not known to be genuine, an analysis would condemn them at once as spurious.

F. W. Morse¹ has reported two butter-fats, from individual cows, giving Reichert-Meissl numbers of 16.5 and 11.2. "The samples were very hard, pale in color, and had an odor resembling that of tallow;" these abnormalities and the phenomenally low figures for volatile acids were attributed to an advanced period of lactation, and the presence of cottonseed products in the feed.

Samples 1 and 6 of Table IV are what might be classified as abnormal, though no note was made at the time of analysis as to any peculiarities in physical appearance. The saponification number of Sample 1 is far below the limit usually assigned to this constant, while the iodine absorption is excessively high; the irregularities of these two figures are explained by the prevalence of gluten feed in the ration.

The saponification and iodine numbers of Sample 6 vary at the opposite extreme; root crops, such as sugar-beets and mangels, predominated in the rations fed to the animals producing this butter, and no doubt account for the unusual figures.

While the butter-fat from the milk of single cows may frequently show abnormalities, such instances are less common with a full herd, since individual differences would be concealed in a general average; nevertheless, such instances do occur. Farnsteiner² and Karsch report the following constants of two butter-fats:

¹ New Hampshire Experiment Station Report (1893), p. 152.

² *Ztschr. Untersuch. der Nahrungs u. Genussmittel* (1898), 16-21; Abstract in *Analyst*, No. 263, p. 38.

	Saponification number.	Iodine number.	Reichert-Meissl number.
I. From 180 cows.....	218.53	49.57	22.80
II. " 25 "	219.74	40.00	22.11

The abnormal chemical constants of these samples were attributed to a very advanced period of lactation; no mention was made as to any anomalies of taste, odor, etc.

Sickness, peculiarities of feed, and advancement in the period of lactation are the principal causes of irregularities in the composition of butter-fat. The subject is one of special interest and illustrates the difficulty, occasionally experienced, of absolutely identifying the character of a questionable butter-fat. It will be of interest in this connection to compare the generally accepted limits for the three constants, used most universally in butter-fat analysis, with the extreme limits, where the names of the observers are bracketed.

	General limits.	Extreme limits.
Reichert-Meissl number.....	20-33	11.2[Morse]-41[Nilson]
Saponification number	220-236	216[Samelson]-245[Fischer]
Iodine number.....	26-38	19.5[Moore]-49.57 [Farnsteiner] [and Karsch]

INFLUENCE OF RATION UPON THE CHEMICAL COMPOSITION OF BUTTER-FAT.¹

Allusion has already been made to the influence of certain feeds upon the chemical constants of butter-fat. Considerable work has been performed at the Pennsylvania Experiment Station along this line, in connection with various dairy-feeding experiments, according to plans of Dr. William Frear; the results of this work have, for the most part, not yet been published. A full discussion and tabulation of these experiments would be foreign to the nature and purposes of the present article, but certain general conclusions from the work may be briefly stated in this connection. The work of others has, in the main, been corroborated; this is true especially as regards the effect of different rations upon the volatile acid figure and iodine absorption. It is to be regretted that so few experimenters, in their work along this line, have reported determinations of the saponification number,—a constant, the value of which in butter-fat

¹ Bulletins 13 and 16, New Hampshire Experiment Station, contain some excellent experiments along this line. For a very full discussion of the subject see article by William Frear in *Agricultural Science*, 7, No. 3, p. 120.

analysis, as it seems of late, has been too greatly underestimated.

Briefly, the experiments conducted here indicate that, while the tendency of certain feeds, of which gluten meal is a type, is to greatly diminish the saponification number and increase the iodine absorption, other rations, such as those consisting of root products, beets, mangels, etc., have precisely an opposite effect; the extreme figures of Table IV, in butter-fats Nos. 1 and 6 were mostly, if not entirely, produced by just such a difference in ration.

It was found that other feeds, such as cottonseed, linseed, and corn-meal, all produced decided effects upon the chemical qualities of butter-fat; the three feeds named, when fed in moderate quantities, showed a tendency to elevate the saponification number, but there was a difference in other respects; while cotton and linseed meal diminished the Reichert number, corn-meal seemed to increase this constant; cottonseed and corn-meal both caused a marked decrease in the iodine absorption, whereas linseed meal produced an elevation in the iodine figure. Great care must be exercised in the interpretation of results from such experiments; other factors, such as the individuality of the cow and the stage of lactation, must not be lost sight of. The precise influence of a particular food upon the composition of the butter-fat cannot, in every instance, be foretold; we may say that the effect will always be more or less a variable quantity, since a great deal depends upon the nature of preceding rations.¹

There is room for much study along this particular line, and further researches are greatly to be desired, not only as regards the effect of different kinds of food upon the chemical qualities of butter-fat, but also as regards that principle of the ration which is most active in producing a given change, as to whether it be of a carbohydrate, an albuminoid, or a fatty nature. The solution of the difficult physiological problem, dealing with the origin and formation of the fat secreted by the lacteal glands, will certainly be promoted by such investigations.

¹ Linseed meal, for example, if fed after a cotton meal ration, would elevate the iodine absorption, whereas, if fed after gluten meal, the iodine number would be diminished.

NOTE.

How to Ignite a Hydrogen Jet with No Possibility of Exploding the Generator.—The following are perhaps fair samples of the directions usually found in text-books and manuals for igniting a jet of recently generated hydrogen gas:

"After the action has continued for a minute or two apply a lighted match."¹

"When all the air is expelled, not less than ten minutes, light the jet of hydrogen."²

"When the gas is coming off freely, light the jet."³

As is well known, with any of the above directions, inexperienced students do continue to explode hydrogen generators with annoying frequency, and it is believed that a method of igniting a jet of hydrogen gas with no possible danger of exploding the generator will be welcomed generally by teachers of introductory and qualitative chemistry.

The following method, used by the writer with his classes for a number of years, is absolutely safe and causes no loss of time whatever:

As soon as the action begins collect the escaping gas in a test-tube, and when it is thought to be full of pure gas, remove two or three feet from the generator and ignite the hydrogen in the test-tube; then immediately *attempt* to light the jet of hydrogen *with the hydrogen flame contained in the test-tube*. If the gas is explosive it will explode in the test-tube and *leave no flame*. If on the other hand a flame remains in the test-tube with which the jet can be ignited, it is certain that the gas in the generator is no longer explosive. Hence, the caution: Never light the hydrogen jet except with the hydrogen flame obtained as just described. The student may try to ignite the jet by this method as often as he wishes until he succeeds, and if the hydrogen is properly generated the jet will be ignited in less than a minute.

UNIVERSITY OF ILLINOIS, AGRICULTURAL
EXPERIMENT STATION.

C. G. HOPKINS.

A New Test for Cocaine.—There are two well-known tests for determining the freedom of commercial cocaine salts from other

¹ Remsen: Introduction to Chemistry, p. 64.

² Newbury: Laboratory Note-Book, eighteenth practice.

³ Shepard: Elements of Inorganic Chemistry, p. 38.

coca alkaloids. These are the permanganate test for detecting cinnamyl-cocaine, and the ammonia test, popularly known as McLagan's test, for detecting the presence of the coca alkaloids which are resistant to permanganate. While it is generally admitted that the permanganate test is sufficient to detect the presence of cinnamyl compounds, chemists have expressed some doubt regarding the value of McLagan's test. The writer has for some time been conducting experiments with the object of finding a substitute for McLagan's test which would allow of the rapid and accurate determination of the presence in cocaine salts of the coca alkaloids not indicated by the permanganate test.

As the result of numerous determinations, I have devised a test based on the fact that the chromates of these alkaloids are much less soluble than cocaine chromate, both in water and in water acidulated with hydrochloric acid. The relative solubility of the chromates in acidulated water is about 1 to 500 in the case of cocaine chromate, and 1 to 5000 in the case of the residual alkaloidal chromates.

I therefore offer the following as a simple and satisfactory method of determining the purity of cocaine salts: 0.05 gram cocaine hydrochloride is dissolved in twenty cc. of distilled water, mixed with five cc. of a three per cent. solution of chromic acid, and to the mixture five cc. of a ten per cent. solution of hydrochloric acid are added. It is advisable to keep the temperature of the solution at 15° C. If the cocaine hydrochloride be pure a clear solution will result. If other than traces of foreign coca bases be present the solution becomes cloudy at once, or in a few minutes, according to the amount of impurity present.

It is advisable to make the test side by side with a specimen of known purity for comparison. GEORGE L. SCHAEFER.

N. Y. QUININE AND CHEMICAL WORKS,
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ON THE OPTICAL ROTATION OF PINEN HYDRO-CHLORIDE.

By J. H. LONG.

Received April 26, 1899.

THE data found in the handbooks concerning the optical properties of this well-known compound, commonly called artificial camphor, are far from being in accord with each other or in accord with the actual facts. The earliest published results making pretense to accuracy are apparently those of Berthelot.¹ The conditions favoring the production of the compound from *l*-pinen or purified French turpentine oil and the physical properties of the finished substance are clearly stated. Some of the succeeding observers seem to have overlooked this earlier work and have published much less carefully controlled data.

I have elsewhere called attention to the production of this body from purified American turpentine,² but consider it necessary to add something to the data there presented, inasmuch as the somewhat misleading statement of Pesci³ and Wallach, and Conrady⁴ as to the inactivity of the product, have passed into the literature. See, for example, Landolt's "Optisches Drehungsvermögen," 2d. ed., p. 556.

¹ *Ann. chim. Phys.* [3], 40, 5 and later.

² *J. Anal. Appl. Chem.*, February, 1893.

³ *J. B.* (1888), 900.

⁴ *Ann. Chem.* (Liebig), 232, 156; *J. B.* (1889), 737.

The product is easily made by passing dry hydrochloric acid gas into turpentine oil, but to obtain it in pure condition it is necessary to employ a turpentine which has been purified by treatment with alkali and subsequent fractionation. The direction is usually given to cool the turpentine by immersing the container in a freezing-mixture, but this is not necessary. The maximum amount of product is not obtained at a low temperature, but at a temperature much above the freezing-point, possibly about 30° C. Inasmuch, however, as the turpentine becomes very warm during the reaction it is necessary to cool somewhat to maintain this temperature in the liquid. Marsh and Gardner¹ state that a high temperature is even better than a low temperature for production of the compound.

To determine the effect of temperature at the time of passing the gas through the turpentine the following experiment was made. Some commercial oil was allowed to stand several days over well-dried potassium carbonate, with frequent shaking, and was then poured off and treated with metallic sodium during a week in the same manner, and practically until all action ceased. The clear liquid remaining was then distilled, the higher boiling portions being rejected. From fresh American oil it is easy to obtain in this way the major portion boiling from 156° to 158°. A liter of the product so obtained which showed the specific rotation,

$$[\alpha]_D = +14.65^\circ$$

was divided into two portions. One was poured into a flask kept cool by ice and salt, while the other was poured into a similar flask, connected with the first but allowed to stand in the air. A rapid current of dry hydrochloric acid gas was bubbled through both flasks during several hours on two days. The separation of the crystalline solid began first in the cold flask, which finally had to be disconnected to allow the gas to pass. In the second flask, which became quite warm during the reaction, 40° or above, crystallization was slow, but in the end fully as much product was obtained here as in the other. Both masses of crystals were collected on filters and allowed to drain thoroughly. They were then dissolved in hot pure alcohol and

¹ *J. Chem. Soc.*, 59, 725 (1891).

recrystallized by cooling. The new crystals were dissolved and crystallized again from alcohol, and the products now obtained were drained thoroughly and dried between porous plates. For polarization tests benzene solutions were made containing exactly five grams in twenty-five cc. The same specific rotation was found for the two products; *viz.*,

$$[\alpha]_D^{25} = +7.17^\circ.$$

The absolute agreement in the rotation values is probably accidental, but it is at least evident that the temperature effect cannot be important, as was indeed pointed out by Berthelot.¹ It may also be noticed that the specific rotation is about half of that of the original pinen, but this fact is without importance, as very different values are found from different oils. Some chemists give much higher values for the specific rotation. Flawitzky, for example², gives values between $+24^\circ$ and $+30^\circ$ for different samples. Marsh and Gardner³ state that the specific rotation is from $+3^\circ$ to $+5^\circ$. Wallach and Conrady⁴ in giving the substance as inactive state that *d*-pinen is much more readily made inactive by hydrochloric acid than is *l*-pinen, but offer no evidence to explain this view. If this were true it is likely that this effect of the acid would be heightened by increase of temperature, but observations, such as given above, show that this is not the case.

In investigations on the pinen from American oil it must be remembered that the commercial turpentine is distilled from the oleoresin from a number of distinct species of pine, and the product, as it appears in commerce, is always, and unavoidably, a mixture. The oil from any one tree undoubtedly contains both *d*- and *l*-pinen,⁵ but from the long-leaf yellow pine and most other common varieties the oil obtained contains *d*-pinen in greatest abundance, while the so-called *spruce* pines of the region around Mobile, and elsewhere, yield an oil richest in *l*-pinen. As the separation of the optical antipodes by fractional distillation is

¹ *Loc. cit.*

² *Ber. d. chem. Ges.*, 15, 5, and Landolt's "Optisches Drehungsvermögen."

³ *Loc. cit.*

⁴ *Loc. cit.*

⁵ This is not the view generally held, it being sometimes assumed that the antipodes are not present in the same plant. See Landolt's "Optisches Drehungsvermögen," Second Edition, page 116.

impossible, it will be recognized that the usual methods of obtaining dextro pinen from commercial American turpentine are entirely fallacious. It may be added here that the separation of the right and left hydrochloride by fractional crystallization appears to be equally impossible. I mixed in one trial fifty grams of a *d*-product, showing $\alpha = +1.25^\circ$ with fifty grams of an *l*-product, showing $\alpha = -7.01^\circ$, dissolving and crystallizing from strong alcohol in two fractions. For the first fraction I found $\alpha = -2.84^\circ$ and for the second $\alpha = -2.85^\circ$, while the mean calculated value of the mixture is $\alpha = -2.88^\circ$. Practically the same result is obtained by precipitating partially by water instead of crystallizing from alcohol. These results are in accord with the observed behavior of antipodes in general, as regards solubility.

Some years ago I distilled six samples of perfectly fresh "spruce" dip, each from a single tree, and found that the oils differed in specific rotation, running from -36.6° to -40.8° . Carefully made fractions from these oils, boiling between 156° and 156.7° , gave specific rotations between -40.1° and -42.5° . These differences cannot be traced to oxidation or other changes due to keeping, because the liquid oleoresins distilled were fresh, were "dip" or first-year products, were sent immediately in sealed tin cans, and were distilled with steam without delay. The differences I believe to be due here and in all other cases to the presence of both *d*- and *l*-pinen in the oil of each tree. That the low rotation of many dextro oils is not due to oxidation-products is easily shown by the fact that these oils suffer but little change through treatment with alkali carbonates or the metals themselves; and further, by the fact that the old and partially dried oleoresins, known as "scrape" products, often yield oils showing as high a rotation as those from the fresh dip products.

Supposing now that the most carefully separated low-boiling fractions of American oil contain both *d*- and *l*-pinens the following experiment may suggest a reason for the low rotation of the hydrochloride from the common oil. A sample of left rotating oil treated with alkali and fractionated furnished a principal portion boiling from 156° to 157° . This showed a specific rotation:

$$[\alpha]_D^{20} = -17.11^\circ.$$

The hydrochloride was made in the usual manner and purified by crystallization from strong alcohol. The dried fractions were dissolved in pure benzene to produce solutions containing twenty grams in 100 cc. Three fractions gave specific rotations :

$$1 \quad [\alpha]_D^{20} = -18.29^\circ$$

$$2 \quad [\alpha]_D^{20} = -18.46^\circ$$

$$3 \quad [\alpha]_D^{20} = -18.21^\circ$$

Essentially the same results were found from alcoholic solutions, and from a solution in benzene containing forty grams to 100 cc., a slightly lower value was found. While the data are insufficient to determine the true specific rotation of the pure substance it is evident that the effect of the acid was not to lessen the activity of the pinen, but to increase it. The best comparison is made by introducing the molecular rotations. For the original this is

$$[M] = -17.11^\circ \times 136 = -2326.9,$$

and for the hydrochloride it is

$$[M] = -18.32 \times 172.5 = -3160.2,$$

from which it appears that on comparing equal molecules the rotation is much increased.

Assuming now that the action of hydrochloric acid on *l*-pinen is to increase rather than to decrease the rotating power while the action on the *d*-pinen is to produce a hydrochloride with nearly the same or probably a somewhat decreased rotation, it is apparent that from a common dextro oil the hydrochloride obtained must necessarily show a lower rotation. It could even follow that a change of sign would result, but I have not yet observed this possible case in any one of the many samples which I have converted into hydrochloride. I have found a specific rotation of less than 1° in several instances. The inactivity of the preparations from dextro American oil described by Pesci¹ and by Wallach and Conrady² may doubtless be accounted for in this manner. If, as Wallach assumes, the *d*-pinen becomes readily inactive under treatment with hydrochloric acid, it would

¹ *Loc. cit.*

² *Loc. cit.*

certainly follow that the hydrochloride from much of the dextro American oil must show a negative rotation. But this is not in agreement with the facts.

Pesci appears to be in error, with others, in giving the melting-point of the hydrochloride as 125° . A careful determination of three preparations from rather large amounts of purified and fractionated oil gives me 131° as the true melting-point, and this agrees with the value given by Riban.¹

My thanks are due Mr. Frank Wright for valuable help in preparing samples of the hydrochloride and in determination of the optical constants.

CHICAGO, April, 1890.

[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 39].

SEPARATIONS OF METALLIC SULPHIDES BY MEANS OF HYDROCHLORIC ACID GAS.

BY J. BIRD MOYER.

Received April 3, 1890.

A NUMBER of quantitative separations have been made in the last few years through the agency of the haloid acids in gas form. With a few exceptions the experiments made in this laboratory and elsewhere required the use of metallic oxides or the salts of oxygen acids. The analogy of sulphur to oxygen in its derivatives led to the conclusion that similar behavior might be expected from the metallic sulphides. Smith and Keeley¹ found that arsenic sulphide, antimony sulphide, and stannic sulphide were completely volatilized in a stream of hydrochloric acid gas and that stannous sulphide, though not volatilized, was changed to stannous chloride. An attempt was made by them to effect a separation of stannic sulphide from stannous sulphide in this manner but it proved unsuccessful. Smith and Field² separated arsenic sulphide from vanadium sulphide quantitatively by this method.

The acid sulphides being volatile in hydrochloric acid gas it was natural to suppose that they might be separated quantitatively from the more basic metallic sulphides. It was hardly

¹ Wurtz's Dictionary, Vol. V, 306 and 312.

² This Journal, 18, 1096.

³ *Ibid.*, 18, 1051.

expected that such a course, though possible, would be pursued in ordinary analytical chemistry, yet it was thought that an investigation of this field might prove interesting. The sulphides for this purpose were precipitated, carefully washed and dried; in some cases, however, to avoid the oxidation which is common in the drying of moist sulphides, they were made by igniting the oxide in a stream of hydrogen sulphide. The dry sulphides were placed in a porcelain boat, weighed and heated in a glass combustion tube, through which was passed a current of hydrochloric acid gas.

Separation of Lead from Arsenic.—The dry sulphide of lead, not proving volatile in hydrochloric acid gas, was mixed with dry arsenic sulphide and heated until all of the arsenic was eliminated. Usually the lead sulphide changed completely to chloride and was weighed as such. It was then taken up in hot water and evaporated down with sulphuric acid and weighed as sulphate with the following results:

Expt.	PbS taken.	As ₂ S ₃ taken.	PbCl ₂ obtained.	PbCl ₂ calculated.	PbSO ₄ obtained.	PbSO ₄ calculated.
I	0.1174	0.1045	0.1350	0.1366
II	0.3230	0.1175	0.3763	0.3758	0.4105	0.4097
III	0.1406	0.1100	0.1630	0.1636	0.1764	0.1783

In Experiment I the chloride dissolved in hot water leaving a small residue of lead sulphide, but no arsenic, which accounts for the low result.

Lead from Antimony.—The experiments with antimony did not yield results which were entirely satisfactory although this sulphide is known to be volatile. In these experiments it was found that the sulphide of antimony volatilized rapidly at first but more sluggishly toward the end, while the last traces were hard to remove. This fact makes it difficult to decide just when the separation is completed. The results obtained with antimony sulphide, prepared in the dry way, were no better. These figures were obtained:

Expt.	PbS taken.	Sb ₂ S ₃ taken.	PbCl ₂ obtained.	PbCl ₂ calculated.	PbSO ₄ obtained.	PbSO ₄ calculated.
I	0.1837	0.2891	0.2296	0.2230
II	0.1294	0.1100	0.1513	0.1505	0.1648	0.1640

Lead from Bismuth.—Bismuth sulphide like the oxide volatilizes slowly in hydrochloric acid gas. The time required de-

pend upon the amount taken. In the first experiment the bismuth sulphide changed in the cold and volatilized at a low temperature, while in the second experiment heat was applied for three or four hours.

Expt.	PbS taken.	Bi ₂ S ₃ taken.	PbSO ₄ obtained.	PbSO ₄ calculated.
I	0.1093	0.1121	0.1389	0.1386
II	0.6741	0.2638	0.8525	0.8550

There was no bismuth found with the lead after the reaction.

Cadmium from Arsenic.—Experiments with cadmium sulphide show that it does not volatilize except at a high temperature, consequently it is an easy matter to remove the arsenic from a mixture of their dry sulphides. The following results were obtained :

Expt.	CdS taken.	As ₂ S ₃ taken.	CdCl ₂ obtained.	CdCl ₂ calculated.	CdO obtained.	CdO calculated.
I	0.1188	0.1143	0.1507	0.1509
II	0.1098	0.1359	0.0976	0.0959

In Experiment II, the cadmium sulphide was not all changed to chloride. The residue was, therefore, made into a paste with hydrochloric acid and pure mercuric oxide, ignited and weighed as oxide. A third experiment was tried using cadmium arsenate which was heated in hydrogen sulphide gas and then in hydrochloric acid gas.

	Gram.
Cd ₃ As ₂ O ₇ taken	0.2497
CdCl ₂ obtained	0.2096
CdCl ₂ calculated	0.2109

The separation was complete in two hours at a temperature of 170° C.

Silver from Arsenic.—Silver arsenate was heated in a stream of hydrogen sulphide until it turned black. A temperature of about 190° C. was required. Hydrochloric acid gas was then substituted for the hydrogen sulphide and the temperature increased from 200° to 250°, when the mixture of silver and arsenic sulphides was visibly attacked. The mass melted, and the arsenic volatilized rapidly, leaving a white residue of silver chloride. Results :

Expt.	Ag ₃ As ₂ O ₇ taken.	AgCl obtained.	AgCl calculated.
I	0.3292	0.3059	0.3060
II	0.5054	0.4684	0.4699

The result in Experiment I is very close to the theoretical. In the second experiment the result is good but shows a slight loss from sublimation. A higher temperature was required in the latter case to start the reaction and a naked flame was applied for a few minutes, which occasioned a faint sublimate of silver chloride just above the boat. The arsenic was found to be completely eliminated.

The above results show that it is not impossible to separate sulphides as well as oxides by means of hydrochloric acid gas. The sulphides of arsenic, antimony, and bismuth may thus be separated from lead sulphide, and the sulphide of arsenic from the sulphides of cadmium and silver. One more volatile sulphide, the sulphide of bismuth, should be included with those already mentioned. This might well be expected as the oxide volatilized in hydrochloric acid gas. This volatility of bismuth affords a method of purifying lead compounds which contain it, as its oxide or sulphide will be entirely removed by the use of hydrochloric acid gas. It is not unlikely that further separations depending upon the volatility of arsenic, antimony, tin, and bismuth sulphides may be made and the number of possible separations thus considerably increased.

The non-volatile sulphides were converted into chlorides with a variable degree of success. This in some cases depended upon the manner of their preparation. An interesting example of this was the behavior of antimony sulphide. A portion of the precipitated sulphide was heated in hydrogen sulphide to render it homogeneous, when it melted, and after cooling slowly in this gas, it crystallized nicely as stibnite. In this form it was volatilized with difficulty.

UNIVERSITY OF PENNSYLVANIA,
March 29, 1899.

THE INCANDESCENT ELECTRIC LAMP AS A SOURCE OF HEAT IN ETHER EXTRACTION.

BY C. G. HOPKINS.

Received March 20, 1899.

AS a substitute for the electric heater recently described by Sammis¹ the writer employs the ordinary incandescent lamp in extraction work. The arrangement of twenty complete

¹ This JOURNAL, 21, 42 (1899).

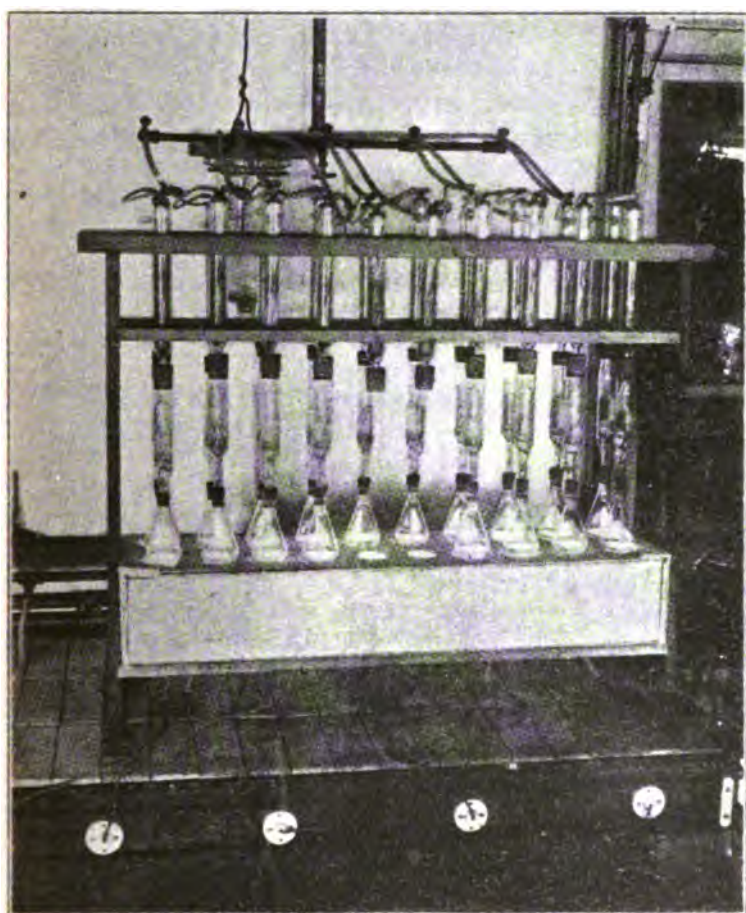
sets of Soxhlet extraction apparatus as is used in this laboratory is shown in the accompanying cut.

Five 110-volt lamps of thirty-two candle-power each are placed in the air-bath, a water-bath not being used. These are sufficient to produce a distillate amounting to about sixty drops per minute in each apparatus. The constancy of the supply of heat from the incandescent lamp is of course all that could be desired, and the fact that about ninety-six per cent. of the electrical energy is transformed into heat indicates the economy of this lamp for heating. The five lamps are connected in parallel and the current turned on or off by a single switch.

The air-bath is a galvanized iron box, thirty-six inches long, eight inches wide, and six inches deep, with double side walls and triple end walls, leaving half-inch spaces in which are placed strips of asbestos paper to decrease the loss of heat by radiation. The board upon which the bath is fastened is also covered with asbestos. The cover of the bath is removable. It contains twenty holes, arranged in two rows of ten each, which are two inches in diameter and whose centers are three and one-half inches apart each way. The lamps are placed seven inches apart, one lamp under the center of the square formed by every four holes. This symmetrical arrangement and the extra precaution taken to decrease the radiation at the ends of the bath should provide practically the same amount of heat for each set of apparatus. By actual count the rates of distillation in the twenty sets varied from twenty-nine to thirty-three drops in thirty seconds.

With the extraction in operation the temperature of the cover of the bath does not rise higher than 75°; but it has been found by experiment that, with all of the holes of the air-bath covered, it is possible to raise the temperature of the lamps to a point at which ether vapor will be ignited; so that, to be assured of *absolute* safety in case one of the flasks containing ether should break, it is necessary to employ a water-bath, the bulb of each lamp being immersed in the water.

It may be noted that the condensers are connected in sets of four, so that five streams of water (each controlled by a separate stop-cock) suffice for the twenty condensers, the water for the entire apparatus being turned on or off by a single valve.



Each condenser may be moved vertically two or three inches without interfering with the flow of water. When in use the condenser is supported by the Soxhlet apparatus; when not in use the side tube resting upon the upper board supports it. (The condensers here shown have already been described in detail.)¹

Several hundred fat extractions have already been made with this apparatus using the electric lamp as a source of heat. It is regularly allowed to run over night and has given perfect satisfaction. Wherever a suitable electric current can be had the incandescent lamp will certainly be found preferable to the gas flame for use in ether extraction, and not only on account of its safety but also because of its greater simplicity, constancy, cleanliness, and convenience.

UNIVERSITY OF ILLINOIS,
AGRICULTURAL EXPERIMENT STATION.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA
UNIVERSITY, No. 9.]

CLASSIFICATIONS OF THE CARBIDES: THEIR MODES OF FORMATION, AND REACTIONS OF DECOMPOSITION.²

BY J. A. MATHEWS.

Received April 19, 1898.

DURING the preparation of an extended "Review and Bibliography of the Metallic Carbides,"³ the author examined with great care the literature bearing upon the chemistry of the carbides. References dating back to 1800 were examined and continuing down to the present, the bulk of the literature being confined to a portion of the present decade. It was found that a great many gaps exist in regard to the details concerning not only the methods of formation and properties, but also concerning the composition of certain compounds which have been from time to time described as binary compounds of carbon with a metal. A great deal of the earlier work seems to be inaccurate, and recent work along this line has not confirmed the existence of some of these earlier described compounds. Enough data has been obtained to warrant the preparation of a fairly thorough classification of these inter-

¹This Journal, 20, 965 (1898).

²Read at the meeting of the New York Section of the American Chemical Society, April 7, 1898.

³Smithsonian Miscellaneous Collections, No. 1090, Washington, D. C., 1898.

esting compounds. The information obtained by reviewing all this mass of literature upon the carbides has been condensed, and is here presented in three tabular statements. The first table is a classification of all the known carbides with their formulas so far as is possible. Doubtful ones are included, but the doubt is indicated by a question mark. In the first and second columns of this table all carbides which have not been made in the electric furnace are bracketed. The classification is based (1) upon the general mode of formation, and (2) upon some distinctions in regard to their decomposition with water or hydrochloric acid. The metals entering into the carbides are classed according to their periodic relations.

Following this table the various modes of formation are classified, and the carbides which have been made by each method are grouped. The last classification is based upon typical decompositions, those reacting in the same manner toward a given reagent being grouped together.

The question marks inserted throughout these three tables suggest many interesting subjects for research and investigation. Perhaps thus calling attention to them will result in some of the uncertain points being cleared up and the gaps in our positive knowledge filled.

I. CLASSIFICATION OF THE CARBIDES.

Peri- odic group.	Formed in dry way by heat.		Formed in wet way.
	Decomposed by H_2O .		Not decomposed by H_2O .
	Decomposed by fusion with caustic and by powerful oxidation. Mostly burn in halogen gases at moderate temperatures.		Decomposed by HCl . Explode at low heat.
I.	Li_2C_2 , $[Na_2C_2, NaHC_2, K_2C_2]$	$[Ag_2C_2, Ag_4C, Ag_5C]$	$Cu_2C_2 \cdot H_2O$, $Ag_2C_2 \cdot H_2O$ $Au_2C_2 \cdot H_2O?$ $HgC_2 \cdot xH_2O$
II.	$[MgC_2?]$ CaC_2 , BaC_2 , SrC_2 , Be_2C_3 (or Be_3C)	$Zn?$	
III.	Al_4C_3 , VC_2 , LaC_2 , ThC_2	B_2C , B_3C	
IV.	$[CeC_2]$ Ce_2C	CSi $[C_2Si]$, TiC ZrC , ZrC_2 $[Pb?]$	
V.		VaC	
VI.	U_2C_3	Cr_2C_2 , $[Cr_4C]$, Mo_2C , W_2C	
VII.	$[MnC, Mn_2C]$ Mn_3C		
VIII.		$[Fe_2C?, Fe_3C?, Fe_4C,$ $Fe_5C_3, Fe_6C]$ Fe_2C $[Ni \text{ and } Co?]$ $[IrC_4?]$ $[Pd?]$ $[PtC_2?]$	

NOTE.—Peculiar double compounds, difficult to classify, find mention in chemical literature; *e.g.*, $Al_2C_2B_{10}$, $3CbC_2 \cdot 2CbN$, $Fe_2(CrMo)_8C_4$, $Fe_7(CrW)_8C_4$, $Cr_2Fe_2C_3$, Cr_3FeC_3 , PtS_2C , Si_3AlC_7 , Si_4C_4S , $Ti_{10}C_2N_8$.

II. REACTIONS OF FORMATION OF METALLIC CARBIDES.

1. From oxides or carbonates of metals heated with carbon in the electric furnace.



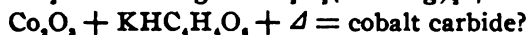
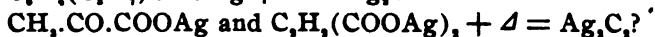
By parallel reactions are also formed the carbides of aluminum, barium, glucinum, boron, calcium, cerium, lanthanum, lithium, manganese, molybdenum, silicon, strontium, thorium, titanium, tungsten, uranium, vanadium, yttrium, and zirconium.

2. Directly from the metals and carbon, $2\text{K} + 2\text{C} = \text{K}_2\text{C}_2$, and similarly, in the electric furnace, carbides of aluminum, boron, chromium, and iron, also at lower temperatures it has been said that carbides of silver, copper, and nickel result, also the carbides of iron in the production of iron and steel.

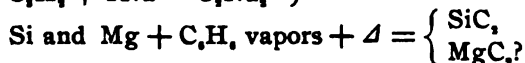
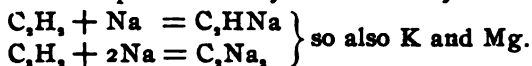
3. By the decomposition of certain organic compounds by heat,

(a) Thiocyanates of silver, bismuth, copper, iron, manganese, lead, tin, and zinc are said to decompose in this way: $\text{Fe}(\text{SCN})_3 + \Delta = \text{FeC} + \text{CS}_2 + \text{N}_2$, provided the operation is done with exclusion of air.

(b) By composition of certain salts of carboxy-acids, *e.g.*,



(c) By the decomposition of hydrocarbons by heated metals,

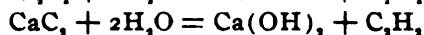
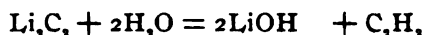


4. Acetylides: formed in wet way by passing acetylene through ammoniacal solutions of silver nitrate, cuprous chloride, and aurous thiosulphate ($\text{Au}_2\text{S}_2\text{O}_3$), or over freshly precipitated mercuric oxide.

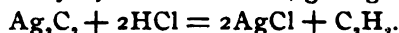
5. The carbides of silicon, titanium, tungsten, etc., have been made from the oxides using calcium carbide as the reducing agent instead of carbon.

III. REACTIONS OF DECOMPOSITION.

1. Decomposed by water giving mostly acetylene: lithium, sodium, potassium, calcium, barium, and strontium carbides.

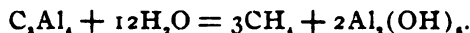


2. Decomposed by hydrochloric acid, giving acetylene.

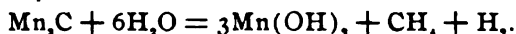


So also copper, mercury and gold (?) acetylides.

3. Decomposed by water yielding methane: aluminum and glucinum carbides.



4. Decomposed by water giving methane and hydrogen: manganese carbide.



5. Decomposed by water giving mixtures of acetylene, ethylene, methane and hydrogen: yttrium, lanthanum and thorium carbides.

6. Decomposed by water giving beside the above volatile products a residue of liquid and solid hydrocarbons; lanthanum, cerium and uranium carbides.

AN EXAMINATION OF COMMERCIAL FLOUR.¹

BY HENRY KRAEMER.

Received April 24, 1899.

IT is now nearly two years since Professor J. U. Lloyd asked the writer to take up the microscopical examination of flour and its adulterants, especially with the view of applying a method, already proposed by the author, at the meeting of the American Pharmaceutical Association in 1894,² for the quantitative determination of corn-meal in flour. A careful preliminary examination of the flour and corn-meal upon the market soon indicated that a detailed study of other cereals, as well as of starch grains, was necessary before reliable and practical results could be obtained. The work upon the starch grain itself was presented, at least in part, in a paper on "The Study of Starch Grains, etc.," to the Pure Food and Drug Congress, January, 1899. It is not necessary here to dwell either upon this study or upon the results of the morphological study of the cereals, as Tschirch and Oesterle have published monographs of

¹ Presented at the joint meeting of the Cincinnati Section with the Columbus Section, University of Cincinnati, April 15, 1899.

² Proceedings of American Pharmaceutical Association, 1894; and *Am. J. Pharm.*, 1894.

the important anatomical features of all the prominent cereals in their "Anatomischer Atlas (Lief. 9-11). Furthermore it was found necessary to consider the various commercial varieties of wheat, the different processes of manufacture, and the by-products and their possible utilization, as well. And in this connection it may be stated that most of the information of this character is quite well known among the more intelligent and progressive millers.¹

GENERAL EXAMINATION.

The flour examined by the author represented all grades from those selling as low as \$1.50 per barrel to the very highest grades, and included the various brands known as "spring wheat," "winter wheat," "Patents," various "blends," "bakers," etc. The first step in an examination of this kind is to determine the grade of the sample under consideration. The following is the procedure then followed by the author:

1. The color test is very useful and may be employed in a dry or wet way. The latter method, however, is preferable and appears to be the one most generally employed by millers as being reliable. In the dry method the samples of flour are placed side by side on a dark-colored board, each sample occupying a space of about one by three inches and less than one-fourth inch in depth. A comparison of unknown samples with a known standard is thus readily made. In the wet method the same procedure is followed, only the board upon which the samples are arranged, is immersed in pure or distilled water at a temperature not exceeding 35° C. In the course of an hour or longer the samples develop a more or less pronounced color according to the grades represented. The author prefers the use of a colorless glass instead of the colored board, as the color effect may be varied by placing the glass upon either a dark or a light surface.

2. The "doughing test" is a very serviceable one and is employed quite extensively by brokers and commission houses. Of course the value of this test is largely dependent upon the personal element or the experience which the operator has had. In the writer's experience the following method gives results which,

¹ A very instructive article of a popular character on this subject, appeared in the March number of the *Cosmopolitan*.

though not conclusive in themselves, are fairly characteristic. On mixing from fourteen to fifteen grams of flour with ten cc. of water at the ordinary temperature, a dough is obtained which is quite cohesive and may be handled without sticking to the apparatus employed. On cool and dry days apparently less flour is required to procure a mass which is not sticky than when the temperature is warmer and the humidity greater. It was thought by the author for some time that the lower grade flours did not require as large a proportion of water to form a dough as the better grades, but the results obtained on treating numerous commercial samples in the foregoing manner would indicate that more likely the opposite is true. However this may be, the dough gives certain prominent characteristics. One of the most prominent, besides that of color, is the firmness of texture which results in some cases. In the better grade flours there results a lighter dough, which is quite elastic, whereas the lower grade flours produce a dough which is more compact.

3. The "gluten" test, which depends upon the washing out of the starch from the mass of dough, is well known to chemists. As to what gluten really is, seems not to be well established. By some writers the gluten is said to be contained in the layer of cells immediately under the pericarp or coat of the grain of wheat. Other authorities claim, however, that in this layer we find aleurone grains and oil and that the gluten is contained rather in the endosperm or reserve cells containing the starch. They ascribe to the protoplasmic threads of these cells the property of gluten. Both are nitrogenous in character and give the same reactions with Millon's reagent for such substances.

The importance of the gluten test appears to depend, according to the writer's experience, more upon its use as a qualitative than as a quantitative test. The physical characters noted above in the examination of the dough, are also found to belong to the gluten mass, obtained as stated by washing the dough with water. A microscopical examination of this glutenous mass furnishes probably the best means for determining the extent to which the flour has been refined. In the better grades of flour we find an almost transparent, delicate, fibrous mass, in which numerous starch grains are imbedded. There are, however, few or none of the hairs of the beard of the grain of

wheat and none of the fragments of the pericarp or coat of the grain. In the poorer samples of flour the hairs and fragments of the pericarp are found to increase in proportion to the decrease of the specimens in quality. From this examination it is very apparent that what is reckoned as gluten may consist of a variety of substances, besides more or less starch, as it is almost impossible to remove the last portions of the latter substance.

It is doubtful whether, as commonly reported, the baker's flours contain more gluten than the patent and other more refined flours of the modern mills. That the lower grades of flour require a greater proportion of water to form a cohesive dough is believed by the author to be due to the presence of a larger proportion of oil in these grades, the oil being contained as above stated in the so-called "gluten" layer along with the aleurone grains. Furthermore, the large quantity of gluten reported as being present in the lower grades of flour is made up, as shown above, of various foreign substances, in addition to the gluten itself.

4. The "baking" test is regarded by some manufacturers and dealers to be the most reliable of any. In determining the grade of a flour test by this the following data are taken into consideration: Weight of flour used, amount of water, yeast and salt, temperature, time required, size and weight of finished loaf, and appearance of same on cutting.

5. The "paste" test may have some significance in determining the quality of flour. The writer finds that if one gram of flour is well mixed with fifteen cc. of water and then gradually heated to boiling, with constant stirring, and allowed to boil for one minute, that the higher grades of flour give a paste which on cooling will scarcely flow at all, whereas the lower grades give a paste which is more liquid in form. In addition the paste in the former case is of a smoother consistency, the latter being characterized by a more or less granular consistency.

6. *Odor*.—Flour having a rather characteristic odor of its own, the presence of foreign substances in it has often been determined by the mere addition of boiling water to the sample. While making some experiments in heating various cereals in glycerin, a very marked odor was detected in a solution contain-

ing corn-meal. This was so pronounced and characteristic that this method was employed for determining the presence of corn-meal in flour. The *modus operandi* is as follows: One gram of flour is mixed with about ten to fifteen cc. of nearly anhydrous glycerin and heated to boiling for a few minutes. If corn-meal be present, an odor similar to that of popped corn is developed. As small an admixture as five per cent. of corn-meal may be detected in this way.

7. In addition to the more or less characteristic general tests above enumerated for determining the value of a flour, the sense of touch may likewise be utilized for this purpose. This method, however, is of value only in the hands of one whose experience has been considerable and whose sense of touch has been especially developed in this direction.

QUALITATIVE EXAMINATION.

The general examination as outlined indicates whether a flour is good, medium, or poor in quality. The more refined flours consist almost entirely of starch grains and a very delicate fibrous material. The cheaper flours contain in addition fragments of the thick-walled cells of the so-called "gluten layer," characteristic long thick-walled one-celled hairs of the beard of the wheat grain and also fragments of the pericarp or coat of the grain. In the still lower grades these tissues are present to a still greater extent.

The main object of this paper being to determine admixtures of corn-meal and flour, it may be stated that this subject must be approached with considerable caution, as this work is based for the most part upon a comparison of the starch grains of corn and wheat. While many of the starch grains of both corn and wheat are quite characteristic, it must be stated, on the other hand, that a large proportion of them so closely resemble each other that in an admixture it is oftentimes practically impossible to distinguish the one class from the other by the methods ordinarily employed. In order to obtain conclusive results, it is necessary that a special micro-physical and micro-chemical study of these starch grains be made. It is only the micro-chemical part of this work that can be referred to at the present time. The following reagents were used for this purpose and the action of them upon the starch

grains of wheat, corn, and potato, was studied for the purpose of comparison :

1. Chloral iodine + iodine solution ; of each equal parts.
2. Chlor-zinc-iodide solution.
3. Chloral solution (saturated), water and glycerin ; of each three and three-tenths parts. To this solution as much iodine is added as the solution will take up.
4. Calcium nitrate solution (thirty per cent.).
5. Chromic acid solution (fifteen per cent.).
6. Saliva.
7. Taka-diastrase (saturated solution).
8. Silver nitrate solution (two per cent.).
9. Sulphuric acid (C. P. acid ninety parts, water ten parts).
10. Sodium acetate solution (fifty per cent.).
11. Potassium hydroxide solution (one-tenth per cent.).
12. Potassium nitrate solution (saturated).
13. Potassium phosphate solution (saturated).
14. Tannin solution.
15. Hydrochloric acid (five per cent.).
16. Water.

Wheat Starch.—Chloral-iodine + iodine solution (No. 1) causes the grains to become at first uniformly blue in color ; swelling of the grains soon takes place and finally alternate light blue and blue layers are observed. Chlor-zinc-iodide (No. 2) behaves similarly to the preceding reagent. Chloral and glycerin solution (No. 3) behaves similarly to No. 1, but the grain is not colored and the lacunæ or fissures are more pronounced. Calcium nitrate (No. 4) produces in fifteen minutes a strong corrosion of some of the grains, and those not acted upon by the reagent in this manner swell in one hour very perceptibly, then show a "tricheten-like"¹ development and in five hours swell enormously and finally burst. Chromic acid (No. 5) produces a similar effect upon the grains, but appears to be more pronounced in its action. Saliva (No. 6) causes in some grains the development of prominent radiations and lamellæ, in others a tricheten-like structure is developed ; in five hours the grains give indications of corrosion, which in the

¹ Arthur Meyer considers the starch grain to be made up of alternate layers of two kinds of acicular crystals (which he calls "tricheten").

course of seventeen to twenty-four hours is very pronounced. Taka-diastase (No. 7) on the other hand, acts very slowly in comparison. In five hours there is little or no effect observable, the tricheten-like structure developing after this length of time and corrosion finally taking place. Silver nitrate (No. 8) has but little action upon the grains at first, in five hours the tricheten-like development appears, and later the grains swell and disintegrate. Sulphuric acid (No. 9) acts almost immediately, causes the grains to become nearly transparent and irregular in outline, and a rapid solution takes place. Sodium acetate (No. 10) causes some of the grains, in the course of five hours, to swell and others to become very much corroded. Potassium hydroxide (No. 11) produces very soon a swelling and rupture of some of the grains and in others the development of a prominent tricheten-like structure, and finally in both a slow corrosion. Potassium nitrate (No. 12) causes almost immediately a swelling and rupture of the grains, or a strong corrosion. Potassium phosphate (No. 13) produces prominent fissures with the subsequent development of rather numerous tricheten-like layers in some grains, in others there is a swelling and rupture of the grains, with finally a gradual corrosive action on both. Tannin (No. 14) produces a swelling of the grains, together with the development of rather large irregular lacunæ, and in five hours the grains become very much swollen and of irregular shape, after which disintegration and solution takes place. Hydrochloric acid (No. 15) causes the appearance of prominent tricheten in some of the grains in a few hours, in others there is a tendency to swell, and both kinds finally divide into two or more parts. Water (No. 16) at a temperature between 50° and 70° C. produces a marked effect upon the grains; those digested at a temperature between 50° and 55° C. for several hours, are swollen, and in many cases are even ruptured; at 60° C. they show a prominent tricheten-like structure, which is scarcely visible at 65° C., and after digestion at 70° C. for one hour the grains become very irregular and swollen and are apparently not further effected by a temperature between 70° and 95° C.

Corn Starch.—Chloral-iodine + iodine solution (No. 1) causes some of the grains to swell in five hours and others to show a tricheten arrangement of the layers; the grains do not appear

to be swollen to the extent that the wheat grains are, and therefore show apparently a deeper color with the iodine. Chlorzinc-iodide (No. 2) brings out immediately the fissure or point of growth, which is in marked contrast to the wheat starch; in the course of several hours the grains swell at one end, the portion showing the swelling becomes light blue, and finally almost colorless, while the other portion remains of a deep blue color; some of the grains finally disintegrate into several portions. Chloral and glycerin (No. 3) causes the appearance of lenticular, somewhat irregular, or more or less star-shaped and prominent lacunæ or fissures, and in the course of twenty-four hours in some grains prominent radiations are developed, whereas in others a marked swelling takes place. Calcium nitrate (No. 4) makes the point of growth more visible as with previous reagents, then strong radiations or a tricheten-like structure develops in some grains, whereas in other grains the fissures develop into large radiating canals, which extend to the margin of the grain, the swelling continuing so that in five hours only the outline of the grain is visible. Chromic acid (No. 5) causes a prominent swelling of the more or less star-shaped point of growth, which continues to such an extent in some cases as to produce a rupture of the grain at one of the angles; in other cases there are numerous radiations, or a tricheten-like structure, developed around the swollen fissures, which finally disappear as the grain swells and breaks down. Saliva (No. 6) acts upon the grain very much like chromic acid and calcium nitrate, only instead of a swelling of the grain we have a rather slow corrosion in the course of forty-eight hours following the pronounced development of fissures. Taka-diastase behaves like saliva, only the corrosive action is more rapid. Silver nitrate (No. 8) causes the formation of prominent and angular fissures, which become more or less circular in outline, and near the periphery prominent radiations may develop. Sulphuric acid (No. 9) produces in some of the grains marked development of an angular fissure which becomes circular or radiating in outline, whereas in others a corrosive action appears to begin at the periphery of the grain, followed by gradual solution of the entire grain. Sodium acetate (No. 10) behaves very much like calcium nitrate. Potassium hydroxide (No. 11) acts simi-

larly on the grain to calcium nitrate and sodium acetate. Potassium nitrate (No. 12) differs in its action on corn very markedly from that on wheat, in that there is a strong development of radiating fissures which extend in many cases to the periphery, whereas in wheat there is a more pronounced swelling of the grains and an irregular corrosive action. Potassium phosphate (No. 13) causes the development of a prominent lenticular, or star-shaped fissure, which increases in size and in seventeen to twenty-four hours there is a complete breaking-down of the grain. Tannin (No. 14) causes also the immediate production of prominent fissures which in five hours develop into large canals, or circular portions, and there is finally a separation of the grain into several parts. Hydrochloric acid (No. 15) causes in some cases the development of large star-shaped or lenticular fissures, and in other cases in the course of but twenty minutes there is a marked swelling of the grain at one point, which continues until disintegration takes place. Water (No. 16), between the temperature of 50° and 70° C., causes certain characteristic features to be developed; the grains, when heated for one and a half hours at 50° C., develop in most cases a rather pronounced circular fissure, in other grains there may be a swelling or lenticular or star-shaped fissure; at 55° – 60° C. the swelling of the grain is more pronounced, and at 65° C. the remainder of the grains show a marked one-layered tricheten-like structure; at 70° C. the markings have disappeared and the grains have become swollen to angular and irregular masses.

In comparing the results of the aforesaid experiments some general observations may be made. We find that we have at least two different kinds of starch grains in each class. The wheat starch grains are either (1) nearly spherical or elliptical in outline without any prominent point of growth, or (2) are characterized by a many-armed fissure looking like the stone cells in tea leaves. The corn-starch grains are either (1) four to six angled and possess a pronounced lenticular or star-shaped fissure, or (2) are nearly spherical with a more or less circular point of growth. Number one in each of these two classes may be said to represent the typical wheat starch and corn starch grain. The tricheten-like structure already referred to appears to be developed by the action of the reagent in less time

and at lower temperatures in wheat grains than is required to produce this effect in the corn starch. Furthermore, a marked difference in size is manifest in the starch grains of corn and wheat when mounted in water and when swollen by the various reagents. Wheat starch grains when examined in water are one to forty-two microns in diameter, the typical grain for purposes of study being about seventeen microns in diameter; when swollen the grains range in diameter from three to seventy microns, the typical being about fifty-three microns. The starch grains of corn when examined in water are from one to twenty-one microns in diameter, the typical grain being about fourteen microns in diameter; when swollen the grains range in size from four to forty-four microns, the typical being about fifty-three microns in diameter.

QUANTITATIVE EXAMINATION.

It is essential before making a quantitative microscopical examination of flour that a general and qualitative examination, as already described, be made. The author, as stated, in the preface of this paper, proposed some years ago a method for the valuation of powdered drugs and foods, by means of the microscope. This was subsequently elaborated in a paper published in 1897.¹ Inasmuch as the method used at that time is applicable to the present work some of the most important details are here given.

(1) The same *reagents* and mounting media are employed in doing quantitative work as were considered in the qualitative examination of the flour.

(2) The quantity of flour to be examined by means of the microscope must represent the sample in every particular; in other words, the *sampling must be done properly* and in accordance with the methods used in the assay of ores. While the quantity to be examined may consist of but a few grams, it must thoroughly represent the lot of flour on which value is to be given.

(3) The amount of sample used in the examination is generally about $\frac{1}{25}$ gram (= 0.0039 gram = 0.06 grain). The quantity of flour may be weighed out, or, what is more con-

¹ See Proceedings of the American Pharmaceutical Association, 1897; also American Journal of Pharmacy, October, 1897.

venient, with practice, a gram is weighed out and divided with a spatula, as follows :

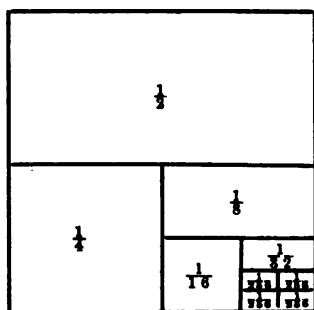


Fig. 1.

$\frac{1}{2}$	= 0.500	gram.
$\frac{1}{4}$	= 0.250	"
$\frac{1}{8}$	= 0.125	"
$\frac{1}{16}$	= 0.0625	"
$\frac{1}{32}$	= 0.03125	"
$\frac{1}{64}$	= 0.0078	"
$\frac{1}{128}$	= 0.0039	"

(4) The cover-glasses used, whether round or square, *should be uniform in size and thickness* for comparison of the mounts of the standards with those of the specimen to be tested.

(5) The *amount of reagent* employed in making a mount must be just sufficient to float the cover-glass, and as few air-bubbles as possible are permitted to be formed.

(6) A *homogeneous mixture* of sample with reagent must be formed before the cover-glass is put down. This is best done by taking the edge of the cover-glass in a pair of forceps and distributing the powder in the mounting media or reagent.

(7) After the mount has been made and the sample examined previously qualitatively, the quantitative estimation of the powder is made. This is based on one or more of the structures or constituents that are characteristic of the sample.

When samples of lower grades of flour are examined the fragments of the pericarp, thick-walled cells of the so-called "gluten layer" and the characteristic hairs of the beard are the structures discerned. In the examination of flour containing corn-meal, the typical starch grains of the latter are selected as a basis for the determination.

The employment of the ocular micrometer, ruled in 100 square millimeters (proposed by the author in 1894), or of the ordinary ocular micrometer (proposed by the author in 1897), is not applicable in the examination of flour as the typical corn starch grains and tissues found in inferior grades of flour are not sufficiently numerous to warrant this procedure. The method best adapted for

the examination of these grades consists in the employment of either the high or low power objective and counting the number of typical starch grains or characteristic tissues which are found in examining five portions of the mount, as indicated by the diagram.

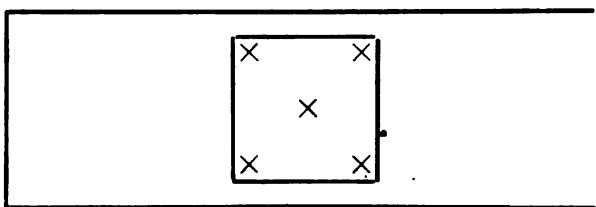


Fig. 2.

When the flour does not contain any corn-meal the low power objective is employed. When corn-meal is present the high power objective (one-fourth to one-eighth inch) is necessary.

(8) *The number of mounts* to be made of the standard and the sample under examination should generally not be less than twelve each. But as two to three mounts can be made upon the same slide, from four to six slides only are necessary for each sample.

(9) If the sample is found to be a mixture, a similar compound, representing the proportions found, should be made up, and the powder under investigation be compared with it.

It is thus apparent that the quantitative results are wholly dependent upon comparisons of an unknown with a known sample. The conditions must be nearly the same in both. The sampling must be done similarly; the same amount of sample must be used in both cases, and no more reagent or mounting media should be used than is necessary to hold the cover-glass without any air being impinged. The same microscope and objectives, as well as other conditions, must be employed to secure even *approximate results*, as this is *all that can be expected at present*.

In the examination of low-grade flours when there is no adulteration with corn-meal, it is not possible to obtain quantitative values, save in terms of some other samples, the market value of which and the extent of refining are known. In the consideration of samples of flour containing corn-meal we find a different

condition. Here the quantitative valuation in terms of corn-meal is based upon the comparison of the unknown samples with prepared samples containing a definite percentage of corn-meal. The count is based upon the number of typical angular corn starch grains with prominent fissures found in the five places of each of twelve mounts, as indicated in Fig. 2. Samples of flour containing from five to ten per cent. of corn-meal have on the average from two to three typical corn starch grains in each mount. When the adulteration varies from ten to twelve per cent. the average number of these starch grains is increased from four to six. In samples containing twenty-five per cent. of corn-meal the average number of typical grains increases to seven, etc., but as the adulteration of commercial flours, according to the author's experience, does not exceed ten to twenty per cent., it is not necessary to proceed further in this direction.

CLASSIFICATION.

From the results of the following experiments a classification of the commercial flours may be made as follows:

I. Those that produce a stiff and cohesive dough in the proportion of fourteen to fifteen grams of flour to ten cc. of water; as, for example, a good spring wheat flour.

II. Those that do not produce a stiff and cohesive dough in the proportion of fourteen to fifteen grams of flour to ten cc. of water.

These may be further divided into the following subclasses:

A. Those that form a smooth, jelly-like paste upon boiling one gram of flour with fifteen cc. of water for about one minute; as, good winter wheat and some of the blended flours.

B. Those in which a more or less granular or liquid paste results. This subclass may be further sub-divided into:

(a) Those which give off an odor of roasting corn when heated in glycerin to boiling for a few minutes, as samples containing corn-meal.

(b) Those that do not give off an odor of roasted corn when heated to boiling with glycerin, as lower grades of flour.

The quality of these flours may be still further determined by a microscopic examination of either the flour or the gluten mass

after removal of the starch, when the presence of fungi and other foreign substances are revealed.

It appears that in certain sections of the country the adulteration of flour, as of other powdered commercial products, is still practiced, yet it may be said that as a rule the article as found in the eastern markets, represents a higher grade of product than has formerly been reported.

The investigations of the writer indicate certain profitable lines of work which are of immediate practical value, and it must be said that much still remains to be done, particularly in the micro-physical examination of the different starches; and the author is of the opinion that as much useful knowledge will be secured by the utilization of the polariscope in this field of work, as has already been disclosed by other methods, the usefulness of this instrument having been demonstrated in the examination of the products made from plant and other fibers.

The author is indebted to Professor Higley, of Northwestern University, and to J. W. Dietrich, of Galesburg, Mo., for assistance in procuring samples; and to Miss Florence Yapple, of the Philadelphia College of Pharmacy, for the performance of much experimental work in the course of the investigation.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 10.]

PREPARATION OF GRAPHITOIDAL SILICON.¹

BY FREDERICK S. HYDE.

Received April 12, 1899.

THE analogy between silicon and carbon in their allotropic modifications, especially the graphitic, and the existence of a crystalline compound of silicon and carbon, known as carborundum, have tended to create doubt as to the purity of graphitoidal silicon, yet the production of the latter seems to be based on reactions favoring the exclusion of carbon.

The usual methods involve the reduction of potassium-silicofluoride with aluminum or metallic sodium; or the reduction of pulverized white sand with magnesium powder.

The method submitted depends on the reduction of finely pul-

¹ Read at the meeting of the New York Section of the American Chemical Society, March 10, 1899.

verized white sand with magnesium powder and the subsequent fusion of the reduction-product with cryolite and aluminum, to form an alloy of aluminum and silicon, from which the latter is obtained on treatment with hydrochloric acid.

For experiment take :

	Grams.
Finely pulverized white sand.....	12
Magnesium powder	3

Mix thoroughly, place in a dry test-tube, supported by a clamp on a ring stand, warm gently, and then commencing at the lower end ignite cautiously with the burner in hand.

There may be a slight separation of the contents due to the expansion of air or moisture, which should be remedied. As the heat becomes concentrated at the lower end, the contents become darker, resulting in a quiet incandescence which creeps toward the upper part, usually completing the reaction with a slight puff. The exterior surface of the test-tube assumes a greenish black lustrous appearance and becomes wrinkled or "buckled" from the heat of the reaction. Remove the contents, which are brownish black in color ; pulverize and mix with a sufficient quantity of cryolite powder.

Introduce the mixture into a small Denver crucible, containing a piece of aluminum (walnut size) on the bottom. The cryolite serves as a vehicle for incorporating the reduction product with the aluminum and as a flux for impurities. Place the crucible in a small gas furnace and apply blast.

As soon as the aluminum liquefies, stir the mass thoroughly with an iron rod. Quite a little stirring is necessary in order that the molten aluminum may be brought into contact with every portion of the reduced mass. Near the final stage, fumes and tongues of bluish flame, like burning zinc, may be observed on the surface. Allow to cool.

Remove the regulus, which should have a brilliant silver-white crystalline surface, and examine the blackened slag for any small globules of alloy. Place the regulus and globules in a porcelain dish or casserole, and treat with warm hydrochloric acid. As the aluminum dissolves, black glistening spangles of silicon separate out of the solution. Decant and wash with clear water. Then wash with alcohol and dry on the filter.

Some employ zinc to form the alloy, but aluminum is preferable for the following reasons not stated in the text-books :

First.—Zinc melts and volatilizes at a comparatively low temperature, before the silicon has a chance to become properly alloyed. It is also difficult to combine the reaction-product with molten zinc, since the latter is heavier and causes the former to float.

Second.—The copious white fumes and blue flame evolved by zinc, even though the crucible be covered and the oxidation minimized, cause large amounts of "zinc wool" to condense on the interior of furnace and crucible, thus interfering with the operation.

Third.—The zinc-silicon alloy is hard and resists solution with hot or cold hydrochloric acid, while the aluminum alloy is readily dissolved.

Fourth.—Zinc tends to produce needle-shaped crystals of silicon, which are not so striking as the graphitoidal spangles obtained from the aluminum alloy.

Graphitoidal silicon resists oxidation before the blowpipe. Under the microscope, by reflected light, the faces of incomplete octahedra are visible in the small irregularly shaped masses. The yield is rarely more than ten per cent. by weight of the silica employed.

There are indications that the element silicon itself, heretofore classed among laboratory curiosities, may become commercially important.

On account of its high electrical resistance, its use in the form of compact rods has already been suggested for electric heating apparatus.

THE COMPARATIVE VALUE OF CERTAIN REAGENTS FOR REMOVING LIME AND MAGNESIA FROM NATURAL WATERS FOR INDUSTRIAL USES.¹

BY MARTIN L. GRIFFIN.

Received May 8, 1899.

IT is only within the past few years, fifteen to twenty possibly, that the purification of water mechanically and chemically has claimed the serious attention of engineers and chemists. Everything is done on such a vast scale to-day and competition is

¹ Read at the meeting of the New York Section of the American Chemical Society, May 5, 1899.

so great that things which were counted of little consequence a few years ago may determine success or failure now. Water contained the same impurities a thousand years ago as it does to-day, but they did not play the same rôle. We all remember when every house had a cistern to catch the pure rain-water from the clouds, when industries sought the source of pure water for their uses. It is the common practice of cities to-day to do this, though there are conspicuous exceptions where extensive filtration and purifying plants are being constructed. Formerly paper-mills were in the habit of digging wells or arching over large areas in the beds of streams and canals in order to obtain a pure water supply. Sponges were used as a filtering medium. Fifteen years ago the company which I continue to serve purified its water for making chemical fiber by pumping the water through a mass of excelsior, which at frequent intervals gave way and passed into the pulp to the confusion of the superintendent, who at first concluded that he had a "bad cook."

These inadequate and unscientific practices are fast giving way to scientific and efficient processes. In 1883 and 1884 J. W. Hyatt and Isaiah Smith Hyatt brought out the modern system of filtration and were the first to claim the use of a coagulant for the precipitation of organic matter in water. One would think that soluble organic matter as it naturally occurs in surface waters would be the most difficult of removal, but with the modern filter using a coagulant this is now accomplished beautifully, leaving nothing to be desired. If we could precipitate and filter out the lime, magnesia, and sulphuric acid as completely as we can remove organic matter, there would be little work remaining for the chemist to investigate in this direction. This, no doubt, has been a favorite theme for speculation with many chemists; however, our inability to do this completely should not prevent putting forth our best endeavors to render a valuable service.

In 1882, Dr. C. B. Dudley obtained a patent for a process using caustic soda for purifying water, claiming as a result that "the lime and magnesia separate as carbonates and the iron and alumina probably as hydrated oxides, etc." This statement assumes that the lime and magnesia exist as bicarbonates only and leaves the subject vague and indefinite.

In 1883 the same author obtained a patent for the use of soda-lime for similar purposes, stating the result of the whole operation to be, "that by far the largest part of the mineral impurities existing in the water previous to treatment are removed."

Doubtless the failure to accomplish all that was expected of this process brought out another claim by Dr. Dudley the next year, which is in effect an amendment to the soda-lime process. In this he adds the use of barium hydroxide, and states that "the result of the whole operation will be that nearly all the mineral impurities occurring in the water, including the sulphuric acid, will be removed from it."

At the first general meeting of this society held in Newport, R. I., in 1890, and which I had the pleasure of attending, Dr. Chas. A. Doremus presented a short paper calling attention to the use of fluoride, particularly sodium fluoride for softening hard waters. At that time the most important statement made was that "the precipitation of magnesium is especially thorough and noteworthy."

In 1893 the same author directed the attention of chemists again to the same subject, perhaps laying more stress on the ability of sodium fluoride to prevent incrustation in feed waters. This statement also appears: "When sodium fluoride is added to waters containing even a moderate proportion of calcium and magnesium salts, a precipitate forms at once." In his patent covering the use of this chemical process, he says: "Since the character of the precipitate produced by a fluoride may be such that it is difficult for a filter to separate it from the water, it may prove advisable to use with the fluoride some chemical capable of producing with the foreign substance in the water a bulky precipitate which shall act mechanically in removing any precipitate of fluoride also produced. Since magnesium fluoride is precipitated in a more flocculent form than calcium fluoride, water containing much magnesium salts may be treated effectually with the fluoride alone, etc. Since caustic soda causes a bulky precipitate when added to waters containing calcium salts, it may be employed with a fluoride for the above-mentioned purpose."

He also says that he has found the use of carbonate and caustic soda with a fluoride more serviceable with certain waters

than when the fluoride alone was used, and that "highly carbonated waters especially seemed to require the use of some caustic alkali." I call attention to these statements, as there seems to be a lack of harmony with the claims made for fluoride. We shall also see that caustic soda in waters containing only calcium sulphate, unless in unusually large amounts, produces no precipitate whatever, and that waters highly charged with carbonates are best suited for the fluoride treatment because of the easy reaction. It was not until I received the January number of the Journal this year, containing an article on "Sodium Aluminate as a Means for the Removal of Lime and Suspended Matter from Waters for use in Boilers," by Prof. Mabery and Edwin B. Baltzley, that I determined to make a systematic quantitative investigation into the value of these and other reagents for removing lime and magnesia from natural waters.

Their method is based on certain reactions which the authors give, all depending on the presence of calcium or magnesium bicarbonate in the waters at the beginning and giving calcium and magnesium carbonates as a final result of the reaction, including the precipitation of the alumina as hydrate.

In regard to waters which contain no carbonates, as for instance, a certain well in Ashtabula, Ohio, cited by the authors, their explanation does not apply. But this is not important. We know that the results depend upon the relative affinities of the bases and acids entering into the reactions and the insolubility of the resulting calcium and magnesium salts.

The authors state that they have made a test comparing the use of different proportions of caustic soda, with aluminate, with the result that "the removal of lime was not much more than half the quantity taken out by aluminate, and the magnesia was not affected." This is certainly a result which chemists could not reasonably expect. The use of sodium aluminate for such purposes is only another way of introducing the strong base sodium, since nothing can be claimed for the precipitated alumina except for its mechanical action. We would therefore look for the same kind of an action whether we were to use sodium hydroxide or aluminate, the free base, however, acting more promptly and with greater intensity.

Also in the case of waters containing only calcium and

magnesium sulphates we would have expected better results in the removal of the magnesium than the calcium, since magnesium hydroxide is far more insoluble than calcium hydroxide.

In the case of one sample the authors say that "air was blown through the solution for a few minutes." No explanation is given for this. Out of some seven samples of water treated, over ninety per cent. of the calcium and magnesium were reported removed from six of them, while the remaining sample, though only an ordinary river-water, gave "unsatisfactory results." It seems that some explanation should have been given for this. The practicability of the process is beyond the scope of this paper.

The reagents selected for my investigation were sodium hydroxide, sodium phosphate, sodium fluoride, sodium aluminate, and barium hydroxide. It will be observed that the primary intent in this work is to introduce a strong, free base, throwing down the insoluble carbonates and hydroxides, of which iron, aluminum, and magnesium are quite insoluble, while that of calcium is easily soluble. We might pause if it were not for this solubility of calcium hydroxide, but unfortunately again the calcium salts are the principal mineral impurities in natural waters, so we pursue our search for a reagent possessing a very strong base and an acid having a greater affinity for the bases calcium and magnesium, and whose salts are insoluble, and we include sodium phosphate and fluoride.

With regard to sodium aluminate, this may be classed with the free base inasmuch as the alumina acts as a very weak acid. I have included it in the test in consequence of the claims made for it by the authors. The principal precipitates resulting from the use of these five reagents are calcium and magnesium carbonates, phosphates, fluorides and hydroxide, iron and aluminum hydroxides, and barium sulphate. With the exception of magnesium phosphate and calcium hydroxide, they are among the most insoluble precipitates we have, but the greater solubility of freshly made precipitates and the greater inactivity of reagents in weak solutions are obstacles to success. The relative affinities also play an important rôle.

The experiments were conducted upon a half liter of water usually, and the results are given in fractions of a gram per

liter. Those who desire to read the results in grains per United States gallon (231 cu. in.), may use the factor 58.38, and for the Imperial gallon (277½ cubic inches) the factor 70. The half liter of the water at the ordinary atmospheric temperature was transferred to a flask of double the capacity, when a slight excess of the reagent to be employed was introduced. The whole was shaken, corked, and allowed to stand on an average of one or two days. The water was then filtered through a close, heavy paper S. S. 598 and the lime and magnesia in solution determined. The reagents employed were normal solutions of sodium hydroxide and fluoride and tenth-normal sodium phosphate and barium hydroxide. The aluminate solution was prepared from a pure aluminum sulphate containing 56.68 per cent. anhydrous sulphate, ten grams to the liter, to which sodium hydroxide was added to alkaline reaction.

In order to obtain some idea of what to expect I began the work with simple solutions of calcium and magnesium. The first was a solution of calcium sulphate containing 0.072 gram calcium oxide, and there remained after treatment with

	Hours.	Calcium oxide. Gram.
Aluminate solution.....	46	0.060
Sodium hydroxide.....	76	No precipitate
Barium hydroxide.....	40	0.060
Sodium phosphate.....	48	0.032
Sodium fluoride.....	28	0.014

Here we observe that all reagents producing the hydroxides are unsatisfactory, while the best results are obtained with the fluoride.

Next a solution of magnesium sulphate containing 0.061 gram magnesium oxide was taken, and there remained in solution after treatment with

	Hours.	Magnesium oxide. Gram.
Aluminate solution.....	25	0.0115
Sodium hydroxide.....	27	0.0349
Barium hydroxide.....	21	0.0183
Sodium phosphate.....	44	No precipitate
Sodium fluoride.....	26	" "

In this case we see that the reagents producing hydroxides are much more successful.

A solution of magnesium chloride containing 0.0558 gram magnesium oxide contained after treatment with

	Hours.	Magnesium oxide. Gram.
Aluminate solution.....	17	0.0082
Sodium hydroxide.....	17	0.018
Barium hydroxide.....	12	No precipitate
Sodium phosphate.....	120	" "
Sodium fluoride.....	28	" "

The latter was concentrated by boiling to one-fifth the original bulk and still no precipitate appeared, showing that no reaction could take place. In this instance only the aluminate and caustic gave results, the former doing particularly well.

We now pass to some natural waters. A sample from the Hudson River at Mechanicsville contains

	Gram.		Gram.
Calcium carbonate.....	0.0234	} equivalent calcium oxide	0.0176
" sulphate.....	0.0110		
Magnesium carbonate .	0.0102	" magnesium "	0.0050

and there remained after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution.....	46	0.0180	0.0048
Sodium hydroxide.....	42	0.0160	0.0043
Barium hydroxide.....	21	0.0176	0.0046
Sodium phosphate.....	24	No precipitate.	
Sodium fluoride.....	24	" "	

In this case none of the reagents were able to effect any appreciable reduction in the amounts of lime and magnesia.

The next is a sample from the middle of Lake Champlain opposite Ticonderoga, and contains somewhat more lime and magnesia, though it is not a hard water. It contains

	Gram.		Gram.
Calcium carbonate.....	0.0341	} equivalent calcium oxide	0.0255
" sulphate.....	0.0156		
Magnesium carbonate	0.0147	" magnesium "	0.0070

and there remained after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution.....	47	0.0256	0.0068
Sodium hydroxide.....	25	0.0256	0.0064
Barium hydroxide.....	25	0.0260	0.0060
Sodium fluoride.....	47	0.0250	0.0057

We draw the same conclusions here as in the case of the Hudson River water.

The next is a sample of tap-water from the city of Niagara Falls and is the Niagara River water. It contains

	Gram.		Gram.
Calcium carbonate....	0.0332	} equivalent calcium oxide	0.0448
" sulphate.....	0.0640		
Magnesium carbonate	0.0272	" magnesium "	0.0129

and there remained in solution after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution.....	45	0.0260	0.0118
Sodium hydroxide.....	46	0.0100	0.0057
Barium hydroxide	45	0.0430	0.0100
Sodium fluoride	46	0.0190	0.0130

We observe that sodium hydroxide gives the best results with fluoride second.

The next sample is from a driven well in Mechanicsville which I will call B. It contains

	Gram.		Gram.
Calcium carbonate....	0.0620	} equivalent calcium oxide	0.0760
" sulphate.....	0.1003		
Magnesium carbonate.	0.0552	" magnesium "	0.0263

and there remained in solution after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution.....	18	0.0650	0.0237
Sodium hydroxide.....	17	0.0160	0.0147
Barium hydroxide	24	0.0260	0.0150
Sodium phosphate.....	17	0.0650	0.0240
Sodium fluoride	46	0.0270	0.0234

Sodium and barium hydroxide give the best results with this water.

The following is also from a local well which I will call D. It contains

	Gram.		Gram.
Calcium carbonate....	0.0398	} equivalent calcium oxide	0.0940
" sulphate.....	0.1760		
Magnesium carbonate.	0.0703	" magnesium "	0.0330

There remained in solution after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution	24	0.080	0.0236
Sodium hydroxide.....	27	0.022	0.0133
Barium hydroxide	24	0.063	0.0029
Sodium phosphate.....	17	0.068	0.0273
Sodium fluoride	71	0.035	0.0338

Again we observe that the best results are obtained with sodium hydroxide, with sodium fluoride second in reference to lime, and barium hydroxide second when we include magnesia.

The next sample is from the Chazy Marble Lime Co.'s quarries in northern New York, and is used in their boilers. It contains

	Gram.		Gram.
Calcium carbonate....	0.1100	} equivalent calcium oxide	0.0850
" sulphate.....	0.0570		
Magnesium carbonate	0.0323	" magnesium "	0.0154

There remained in solution after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution	63	0.0670	0.0136
Sodium hydroxide.....	40	0.0150	0.0111
Barium hydroxide	41	0.0240	0.0115
Sodium fluoride	40	0.0170	0.0115

In this case sodium hydroxide and sodium fluoride gave nearly equally good results.

The following sample is from a well fourteen feet in solid rock near Lake Champlain in Chazy, N. Y. It contains

	Gram.		Gram.
Calcium carbonate....	0.1818	} equivalent calcium oxide	0.1140
" sulphate.....	0.0148		
Magnesium carbonate.	0.0520	" magnesium "	0.0248

and contained in solution after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution	88	0.0720	0.0208
Sodium hydroxide.....	42	0.0140	0.0186
Barium hydroxide	40	0.0300	0.0146
Sodium fluoride	42	0.0220	0.0172

Three out of the four reagents gave very satisfactory results.

The next is a sample of mine water from the Coxe Iron Mfg. Co., at Drifton, Pa., and contains

	Gram.		Gram.
Ferrous sulphate.....	0.0440	equivalent ferrous oxide	0.0208
Calcium sulphate.....	0.0534	" calcium "	0.0220
Magnesium sulphate.....	0.1554	" magnesium "	0.0518
Free sulphuric acid.....	0.1450		

and there remained in solution after treatment with

	Hours.	Ferrous oxide. Gram.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution ..	71	trace	0.0200	0.0516
Sodium hydroxide...	16	none	0.0220	none
Barium hydroxide....	16	"	0.0220	0.0064
Sodium fluoride.....	112	No trace of any precipitate		

showing that this reagent was of no use. The sulphuric acid was not determined. We notice that sodium and barium hydroxide gave very satisfactory results. Barium hydroxide would doubtless be preferred, as it would largely remove the sulphuric acid.

The following sample is from the mouth of Onondaga Creek, Syracuse, N. Y., and contains

	Gram.		
Total solids.....	1.6200		
Sodium chloride	0.6550		
Magnesium chloride	0.0254	} equivalent magnesium oxide	0.0298
" carbonate...	0.0493		
Calcium sulphate.....	0.2176	" calcium "	0.3480
" carbonate.....	0.4614		

and contained in solution after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution	98	0.0840	0.0014
Sodium hydroxide.....	17	0.1280	0.0043
Barium hydroxide.....	136	0.0260	0.0028
Sodium fluoride	117	0.0420	0.0288

In this case barium hydroxide gave the best results, with sodium fluoride second, in reference to lime.

The last sample is from the magnesian lime quarries of the Snow Flake Lime Co., Bowling Green, Ohio, and contains

	Gram.		Gram.
Calcium carbonate	0.0870	} equivalent calcium oxide	0.2080
" sulphate	0.3868		
Magnesium carbonate.	0.1662	" magnesium "	0.0792

and contained in solution after treatment with

	Hours.	Calcium oxide. Gram.	Magnesium oxide. Gram.
Aluminate solution	63	0.0080	none
Sodium hydroxide	16	0.0090	0.0018
Barium hydroxide	16	0.0680	0.0064
Sodium fluoride	21	0.0250	0.0597

In this case we obtain the best results with the aluminate, but the treatment with sodium hydroxide follows so closely that practically there is little difference. The use of barium hydroxide and sodium fluoride are not so satisfactory.

In this work I have endeavored to get samples of characteristic and representative natural waters, such as are commonly met with in the industries, and think the ground is fairly well covered, so that the deductions to be made shall be true and useful.

We note first the limit to which we are able to purify waters in this way, and within what limits we are able to effect a reduction in the amount of earthy substances, by the use of any of the above reagents. The Hudson River contains 0.0176 gram calcium oxide and 0.005 gram magnesium oxide. These amounts we cannot reduce. Lake Champlain, containing 0.0255 gram calcium oxide and 0.007 gram magnesium oxide, could not be reduced, but increasing amounts above these figures show a reduction by one or more of the reagents. I conclude, therefore, that waters containing from 0.020 to 0.025 gram calcium oxide and from 0.005 to 0.007 gram magnesium oxide cannot be purified appreciably, although we observe that frequently the amounts of these impurities can be reduced below these limits in the case of waters highly charged, which is a favorable feature of the work. As regards the removal of calcium carbonate, the most effectual reagents are sodium hydroxide and sodium fluoride, and in some cases we observe that the aluminate solution gave particularly good results as in the last sample, but I will refer to this again. The best results show a reduction in the amounts of calcium oxide of 0.008 to 0.010 gram. It appears also that waters containing a large propor-

tion of calcium sulphate with carbonate can be successfully treated with these reagents as in the case of limestone quarry waters. Barium hydroxide did not prove as effective as I anticipated in the removal of lime.

As regards the removal of magnesium salts, we observe again that sodium hydroxide averages best, with barium hydroxide following very closely, while aluminate solution takes third place, and sodium fluoride produces practically no results on any of the samples. Sodium phosphate was so unpromising from the start, and the removal of the phosphoric acid from the water after treatment added so much to the labor of the work, that I abandoned its use.

We cannot conclude, however, that sodium hydroxide is the best reagent for all waters. Sodium fluoride is much to be preferred in waters containing calcium sulphate and chloride, and is of no value in the removal of magnesium salts.

Barium hydroxide is most serviceable in the treatment of acid mine waters and gave very satisfactory results in the case of Onondaga Creek water, the character of which may be seen from the analysis.

Referring back to the references in the early part of this paper, we are able to place definite limits to Dr. Dudley's processes and to know how far they may be useful. Dr. Doremus' claims for sodium fluoride for the precipitation of calcium salts are fairly well established, but for the precipitation of magnesium salts it is a failure, and for the removal of iron and magnesium very questionable. In my experiments with sodium aluminate I endeavored to follow the suggestions of Prof. Mabery, using somewhat less than the theoretical amount of the combined sodium oxide (Na_2O) in the aluminate necessary to replace the bases lime and magnesia, although the reason for doing this is not plain to me. In every case the action of the aluminate was comparatively slow, and in the case of the lime salts did not give satisfactory results or meet the claims of its authors. It proved more effectual in the removal of magnesium salts, which was to be expected.

I desire to refer to the composition of the aluminate reagent before the subject is left. I prepared this reagent as Prof. Mabery directs, from sodium hydroxide and aluminum sulphate,

from which it will be seen that the available sodium oxide in combination with the alumina is but a small proportion of the composition of the reagent, there being three inert molecules of sodium sulphate to one of sodium oxide beside the alumina. I have no doubt this exerted some influence on the sample of water to which the reagent was added in causing a more complete precipitate of lime and magnesia in some cases.

It would be better to prepare this reagent from pure alumina and sodium hydroxide. As it is, the results are comparable with those reported by Prof. Mabery.

If this reagent could be made as effective in simple practice as the authors claim, leaving practically no alumina in the filtered water, its discovery would prove to be of immense value at once.

In conclusion I would say that there is little doubt but that satisfactory reagents and means will soon be discovered whereby all objectionable waters may be successfully treated at comparatively small expense.

Later I may have something further to contribute to this end.

REVIEW.

THE RETORT COKE OVEN AND THE CHEMISTRY OF ITS BY-PRODUCTS.

There is no innovation into the realm of metallurgical science, these last days of the nineteenth century, which will affect more widely and will, one might say, so revolutionize the whole system of iron- and steel-making in this country as will the introduction of the retort oven for the production of coke, with the simultaneous recovery of the by-products, tar, ammonia, benzene, cyanides and illuminating and fuel gas.

Think of the devastation in the beehive coke oven districts for the year 1897. One has only to take the government statistics of the coke manufactured in this country for 1897 and put opposite it the coke to be made from the same coal in retort ovens of the Semet-Solvay type together with the long list of valuable by-products obtainable, to see the vast amount of valuable material destroyed annually by the present system of coking coal in beehive ovens, and to realize the extent to which humanity has been deprived of what rightly belongs to it. The figures below will illustrate what was actually obtained from the beehive coke ovens in the United States from 22,140,000 tons of

coal in the year 1897, and what would have been obtained if the same coal had been coked in retort ovens :

	Beehive ovens.	By-product ovens.
Tons coal coked.....	22,140,000	22,140,000
Tons coke produced	13,288,984	15,940,000
Value of coke at \$2 per ton	\$26,577,968	\$31,880,000
Value of tar.....	4,428,000
Value of ammonia	8,856,000
Value of cyanides	8,020,000
Value of benzene.....	4,428,000
Value of gas (surplus), 22,140,000 X 4000 = 88,560,000,000 cubic feet at 10 cts	8,856,000
Total	\$26,577,968	\$66,468,000
Difference in favor of by-product ovens \$39,890,032.		

It will be seen by these figures that the saving in coke alone is over 2,600,000 tons, having a value of over \$5,000,000.

These comparisons are made to enable one to comprehend more clearly the immense waste coexistent with the production of coke by the beehive process. The fact is duly appreciated that should all, or a considerable portion, of the coke now made in beehive ovens become the product of retort ovens, the price of the by-products would be greatly diminished.

It will not be long ere the most important blast-furnaces and steel plants throughout the country will be supplied with their own by-product coke ovens, the coke going directly from the quenching car to the blast-furnace without handling, and the surplus gas being used for heating the various furnaces in the steel plant.

Natural gas is giving out. The people, having become accustomed to its conveniences will never go back to the use of coal. They must have a gaseous fuel as a substitute for natural gas.

Boards of health and sanitary organizations are crying out continually against the filthy and unhealthy condition of our cities, arising from the consumption of so much soft coal. There is no longer any comfort in a home in or near a manufacturing city. Travel on steam trains is almost unbearable in certain seasons because of smoke and soot from the engine. What is the remedy? It is the retort coke oven. Retort ovens in the future will also be built in the vicinity of large cities for the production of domestic coke and illuminating gas. Not only will fuel gas be furnished at very low figures, but illuminating gas will be sold at twenty cents per thousand. No smoke will be seen issuing from chimneys and polluting the city and country for miles about, but coke will be the fuel unless gas is used. Stationary steam engines will be a thing of the past, and gas engines up to 1000 H.P. will be substituted, with less cost for power, on account of the low price of fuel gas. Traveling will

be a pleasure for coke will be used in the locomotive, in the place of bituminous coal. But what is to be done with the huge amount of tar recovered? As the production of tar increases, the price must necessarily fall and the lower price will extend the field of consumption. It is only a question of further experimentation and research to successfully incorporate pitch into pavements; lowering the price of "dead oil" will increase the amount of creosoting of timber; there is always the value of tar as a fuel. Millions of tons of the anthracite culm of Pennsylvania and the slack of Ohio, which are now of no value, will, before long, be made into briquettes, thereby consuming thousands of tons of pitch.

But what will we do with so much ammonia? This will be a God-send to the farmer, whose fields are now crying for more nitrogen. His barnyards do not furnish enough of it, and fertilizers are now too expensive. His crops are continually drawing on the nitrogen of the soil, and it must be replaced. In England alone, 120,000 tons of nitrogen annually are abstracted from the soil by vegetable growth, wheat absorbing 37,000, barley 27,000, and oats 57,000 tons. This nitrogen, at present, is principally furnished by the niter beds of Chili. This source in time must fail—England's recourse will be to the nitrogen of her coals which will be coked about her large cities, to be no longer shrouded in black clouds of smoke which obscure the noon-day sun and pollute the atmosphere to that extent that many a man is brought to death's door before his time, and others eke out a half-dead and half-alive existence.

The ammonia formed will be converted into ammonium sulphate, which will largely replace sodium nitrate for fertilizer purposes, and in this country the price will be so reduced as to enable the farmer to use large quantities of it.

Cheap domestic coke or fuel gas from coke ovens will be the only salvation for England's large cities.

Liebig certainly was right when he said, first, "In order to preserve the fertility of the soil, there must be kept in that soil the elements necessary for plant life; second, every crop takes out a portion of these elements. Part of that taken out is added again from the atmosphere, but a part never is restored unless it is put there by human means; and third, the fertility of a soil remains unchanged if all the elements of fertility are restored to it; and fourth, the manurial product of a farm never can restore all the elements of fertility to the soil."

Once a plentiful supply of benzene, toluene, etc., is assured in this country, the aniline color manufacturer will succeed.

A cheap and plentiful supply of cyanides will enable mining engineers to work gold fields which now cannot be successfully worked.

HISTORICAL.

It is about fifteen years since the retort coke oven became a factor in the production of metallurgical coke. The now nearly perfect oven is the result of gradual development from very crude and imperfect ones. There are two types of retort ovens, one in which the horizontal flue is the characterizing feature, and of which class the Semet-Solvay oven is the chief exponent; the other type, in which the heating flues are vertical, is represented by the Otto-Hoffman oven. The first Semet-Solvay ovens, six in number, were experimental and built in 1882, near Mons, Belgium. After a trial of two years the practicability of the system was satisfactorily established and more ovens were built annually, and from 1892 the number of Semet-Solvay ovens has greatly increased, so that at the end of 1897, ovens of this system numbered over 1300. The first in this country were built at Syracuse, in 1892, twelve at first, to which thirteen more were added later. These have been running constantly ever since, with slight repairs.

There are at present in operation on this continent of the Semet-Solvay type, 25 ovens at Syracuse, N. Y.; 50 ovens at Dunbar, Penna.; 25 ovens at Sharon, Penna.; 120 ovens at Ensley, Ala.; 60 ovens at Wheeling, W. Va.; 10 ovens at Halifax; 7 ovens at Boston, Mass. The others are distributed throughout Germany, France, England and Belgium, principally in Belgium where they are very successful in coking low volatile coals, which, in the beehive oven, will not make coke.

DESCRIPTION AND OPERATION OF A RETORT COKE OVEN.

A description of a single isolated Semet-Solvay oven would be as follows: A space five feet, six inches high, sixteen to twenty inches wide, and thirty feet long, is enclosed on both sides by hollow fire-brick tile in three tiers superimposed, placed horizontally. These tiles are about three feet long and when placed end to end form a flue through which the gas, after being treated for removal of the by-products, travels and meets the air for combustion.

The gas is admitted at the ends of the top and the second flues, with a suitable amount of air which has been previously heated by the waste gases going to the chimney flue. At one end of each flue is an opening in the bottom through which the gas passes to the next flue below, the gas and flame passing through the entire length of the flues and finally to the chimney flue.

REVIEW.

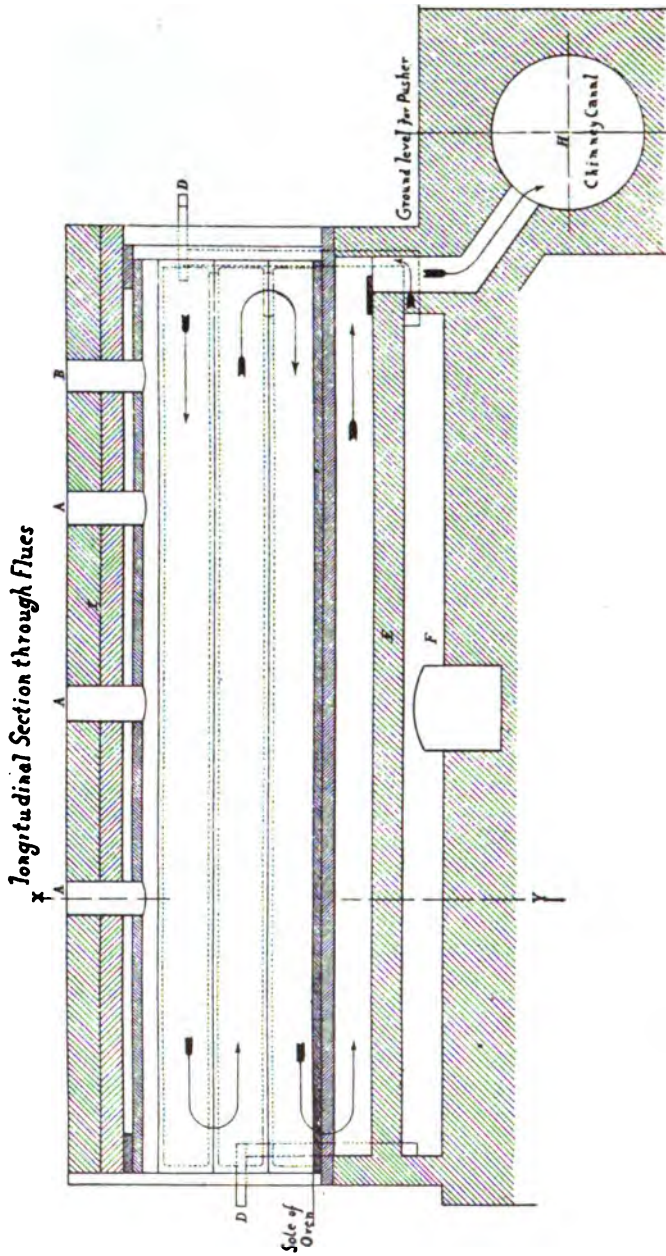


Fig. 1.

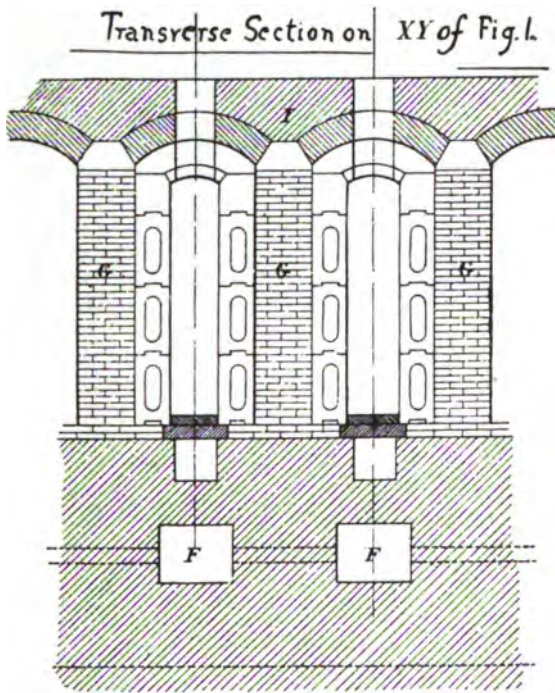


Fig. 2.

The air for combustion is drawn by the chimney draft through a flue, where it is heated by the gases of combustion passing in a flue below the oven, to a temperature of 200° – 300° C. The air is admitted and regulated by means of dampers so nicely, and the gas is under such perfect control, that combustion takes place with the minimum amount of air, and the temperature of flues may be maintained as one wishes from 900° – 1400° C.

The waste gases, still of about 700° – 800° C. temperature, pass under boilers in the by-product plant, which make all the steam necessary to operate all the machinery about the plant, and furnish steam for distillation of the ammonia recovered. From the boilers the waste gases go to the chimney at about 250° C.

The coal, after disintegration, is elevated into bins above the ovens from which, by withdrawal of a slide, coal-cars or "larrys" are filled and are then run out on tracks on the top of the ovens and the coal is charged through three holes. One "larry", holding 3,200 lbs. of coal, is charged to each hole. The total charge therefore is 9,600 lbs. of coal to an oven. The time re-

quired for discharging and again filling and closing up is about fifteen minutes.

The coal after being charged in the oven is then leveled off by means of long hoes put through a hole in the top of the doors at each end of the oven. The doors at both ends when closed and plastered up with fire-clay are practically air-tight.

The time required for coking depends upon the quality of the coal, and the width of the oven. Pocahontas coal for instance, containing nineteen per cent. volatile matter, may be coked in twenty hours in a Semet-Solvay oven, sixteen inches wide, whereas, Connellsville coal, containing thirty-two per cent. volatile matter, in the same oven would require twenty-four hours to properly coke it. If the oven is twenty inches wide, six hours more, or thirty hours, are necessary to completely expel the gas from Connellsville coal. It is a fact also that two coals containing the same percentage of volatile matter may require different lengths of time for the expulsion of the gas. Though the percentage of volatile matter is the same in the two coals, this volatile matter is made up of different percentages of oxygen, hydrogen, and carbon, and because of this difference the gas is expelled with greater or less difficulty.

An important feature in the construction of the Semet-Solvay oven is that the hollow tiles forming the walls of the oven are entirely independent of the side walls, made of fire-brick, which carry the huge mass of brickwork, coal-cars, etc., above the oven proper, and thus relieve the tile from all strains and thrusts, which would have a tendency to displace them, causing leaks, which would deleteriously affect the gas and other products. Because of the freedom from burden, the oven sides of the tile may be made much thinner than they otherwise could, resulting advantageously in conducting the heat from the flue where the combustion of the gas takes place to the mass of coal in the oven. The thick side walls and mass of brickwork above serve to hold the heat, giving it up to the oven during the time of discharging and charging, thus preventing any chilling of the oven. An expansion chamber above the oven permits the tile to expand without affecting the main body of brickwork.

The gas leaves the oven under neutral or a very slight back pressure and is drawn by an exhaustor through a hydraulic main, similar to that used in gas-works, where it is washed free from dust and is partially cooled.

From the hydraulic main the gas goes to large condensers where the gas is cooled by water to 30°C. From the condensers the blower forces the gas through the washer, or scrubber, where the last traces of ammonia and tar are removed. The gas is now divided, such portion as is necessary going back to the

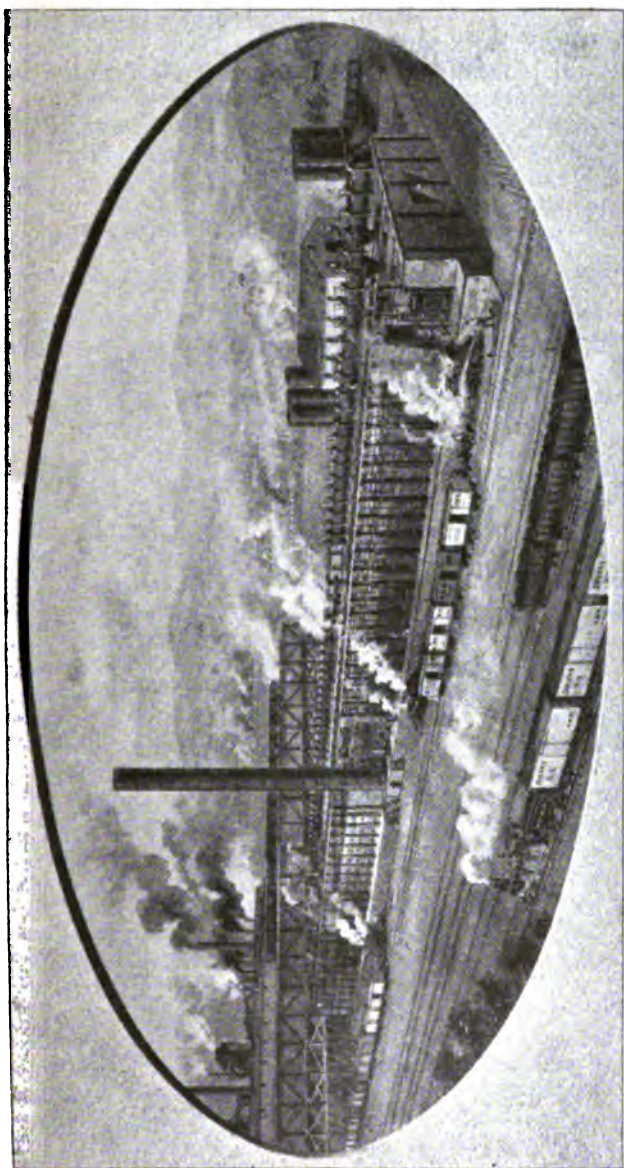


Fig. 3.—Fifty ovens at Dunbar, Pa.

oven flues to keep up the heats, the balance being used wherever fuel may be required.

When the coal is coked, a valve on the uptake pipe shuts off all connection to the hydraulic main; the doors are swung open, or raised, the mechanical ram is put in operation and slowly forces the coke out of the oven, the coke dropping in a thin layer into an inclined car made of iron bars, and a stream of water quenches the coke. The coke holding one and one-half to two and one-half per cent. of water is then elevated for use in lime-kilns or furnaces, or loaded into cars for shipment.

CONTROLLING THE TEMPERATURE OF THE FLUES.

By means of valves on the pipes bringing the gas to the flues for combustion, and by dampers in the air inlets, and by regulation of the chimney draft, any temperature may be obtained, from 900° to 1400° C. The temperatures of the flues are determined by means of the Le Chatelier electrical pyrometer, manufactured by Messrs. Kiser & Schmidt of Berlin, which is a platinum rhodium couple in a porcelain tube which produces a current on exposure to a high temperature and this current is measured by a galvanometer. Another pyrometer which has given good satisfaction is the Callender and Griffiths electrical pyrometer, which depends on the resistance offered by high temperatures to a current from a small battery. Fine platinum wires, through which the current passes, are heated inside a porcelain tube and are in connection with a galvanometer which indicates the temperature. The instrument is favorably spoken of by Lord Kelvin and was used by Messrs. Heycock and Neville in determining the melting-points of gold, silver, and copper.¹

While these instruments have been found very useful to determine accurately the temperature of the flues, they are too delicate to be left in other hands than the expert. As a substitute the Seger cones enable the foreman or workman to judge very closely of the temperature. A round steel rod, six feet long, with three grooves at the end, each large enough to hold a cone, is thrust through a peep-hole in the end of the flue. After fifteen minutes exposure to the heat the cones are removed and their condition noted.

Another instrument made use of by the foreman in charge of the ovens is the telescopic pyrometer of Messrs. Mesuré & Nouell, which seems especially well adapted for coke oven work. The telescope is directed through the peep-hole against the oven side of the tile, and by the degree of incandescence the temperature is determined. Within the tube of the telescope is a polar-

¹ *Chem. Soc. Trans.*, February, 1895. See also for description: *Phil. Mag.*, July, 1891, and January, 1892. *Journal Iron and Steel Institute*, No. 1, 1892. Also a paper by Profs. Dewar and Flemming: *Phil. Mag.*, 1893.

izer, a piece of quartz, and a decomposer. By rotation of the decomposer when viewing the incandescent object, the color changes from green to red, and between these two a gray-lemon tint is seen. This is the sensible shade and the one to observe. A graduated scale on the disk shows the degrees of rotation; a scale of temperatures corresponding to these degrees is given with the instrument.

By means of this telescopic pyrometer the foreman determines the temperature of the flues, and by proper adjustment of gas, air and draught without difficulty maintains the desired temperatures, which are:

Top flue.....	800°- 900° C.
Middle flue.....	1150°-1250° C.
Bottom flue.....	1050°-1150° C.

COMPARISON OF RETORT COKE AND BEEHIVE COKE.

Because of the widely different conditions under which coke in a by-product oven, and a beehive oven is made, one would naturally expect a difference in the appearance and physical characteristics of the two cokes. The heat stored up in the walls of the retort oven is immediately given up to the coal as it is charged and distillation begins, and proceeds horizontally to the center of the oven, the coal in the center of the oven not reaching a high temperature until the latter part of the time of coking. As a result of this heating from the sides, and a slight swelling or expansion, the coke in a soft state is compressed by the walls slightly, and makes that portion of the coke next the oven wall for about one inch quite dense and of little porosity, while the coke in the center presents a highly cellular appearance, and is more or less spongy; the portion between is hard, dense, and of the customary cellular structure of beehive coke. The coke shrinks away from the oven, thus making it possible for the ram to discharge it; it also separates longitudinally in the center. The thickness of the coke on either side of the center is six and one-half to seven and one-half inches, of which about one and one-half inches is extra dense, and from nothing to one inch in the center is spongy.

The total cellular space of retort coke is practically the same as that of beehive coke, and it is able, because of its strong cellular walls, to bear fully as great a burden in the blast-furnace.

The following table shows determinations of cellular space, specific gravity, etc., of coke made from Connellsville coal in Semet-Solvay ovens, and for comparison are given similar tests of beehive coke for the same coal. It will be seen that cubes taken from that part of the coke near the oven wall contain less percentage of cells and have greater weight per cubic foot than any other part of the coke. The average determinations of the cubes

taken from the center portion of the piece of coke do not vary greatly from the standard Connellsville coke.

The following is a table of physical tests arranged according to Mr. Fulton's plan:

	Grams in one cubic inch.		Pounds in one cubic foot.		Percentage by Volume.		True Sp. Gr.
	Dry.	Wet.	Dry.	Wet.	Coke.	Cells.	
<i>Standard Connellsville Beehive.</i>							
	12.51	21.62	47.69	82.20	43.93	56.07	17.4
<i>Connellsville Semet-Solvay Ovens.</i>							
Outside piece..	14.39	23.27	52.47	88.64	52.47	47.53	1.87
"	18.57	25.32	70.71	96.31	59.85	40.15	1.84
Average,	16.48	24.29	61.59	92.47	56.16	43.84	1.85
Center piece...	12.55	20.81	46.17	79.24	45.88	54.12	1.79
"	15.02	23.09	57.19	87.90	50.47	49.57	1.83
"	15.95	25.27	60.85	97.01	47.09	52.91	1.88
"	15.18	24.87	57.81	94.66	45.31	54.69	1.89
"	14.97	23.32	57.00	88.78	49.30	50.70	1.84
Average,	14.92	23.47	55.8	89.51	47.61	52.39	1.84
<i>Connellsville Beehive.</i>							
No. 1.....	11.93	21.18	45.41	80.61	42.57	57.49	1.74
No. 2.....	14.00	24.16	53.30	91.98	43.39	56.61	1.80
No. 3.....	15.07	24.61	57.37	93.70	45.82	54.18	1.80
Average,	13.66	23.31	52.02	88.72	43.92	56.09	1.78

While distillation in the retort oven proceeds horizontally from the outside to the center, in the beehive oven distillation begins at the top and proceeds vertically, and the coke resulting is taken out in long, slender pieces, whereas the product from retort ovens is in large square chunks.

SIR LOWTHIAN BELL'S EXPERIMENTS.

Many years ago, when the first retort coke was put on the market in England, Sir Lowthian Bell made some experiments by which he proved that retort coke would not answer for blast-furnaces; because of the soft nature of the coke the ascending carbon dioxide in the furnace would be converted to carbon monoxide by the carbon, thus diminishing the quantity of carbon which would reach the lower point in the furnace where it was to do its work. It is true that his experiments did show a considerable conversion of carbon dioxide to carbon monoxide when hot carbon dioxide was passed over retort coke in a glass tube. The coke he used, made in a Simon Carvé oven, was certainly in no respect similar to that now made in the Semet-Solvay ovens, for we have many times repeated Sir Lowthian Bell's experiments, using retort coke from Connellsville coal, and for comparison with it have experimented with the standard Connells-

ville coke, and have obtained practically the same results with both cokes. The following are some of these results :

Ten grams of the coke, size of mustard seed, was placed in a combustion tube and then in a furnace and heated at a red heat for one hour. During this time five liters of dry carbon dioxide was passed over the incandescent coke. At the end of the experiment the coke was again carefully weighed and the loss in weight determined with the following results :

SOLVAY COKE.

	Loss of carbon. Per cent.
Experiment No. 1	0.55
" " 2	0.35
Average	0.45

BEEHIVE COKE.

Experiment No. 3	0.46
" " 4	0.49
Average	0.47

It will thus be seen that the two cokes, as far as the action of the hot carbon dioxide is concerned, are practically the same.

Tests were also made of retort coke and beehive coke from Buffalo, Rochester and Pittsburg coal. Average samples were used in both cases.

By these tests it will be seen that there was less conversion of carbon dioxide to carbon monoxide with the retort coke than with the beehive coke.

CARBON DIOXIDE COKE TEST.

Kind of coke.	Weight used. Grams.	Tempera- ture °C.	Time. Hours.	Volume CO ₂ . cc.	CO ob- tained. cc.	CO per 1000 gms. coke. cc.
Beehive, B. R. & P. 13		900° C.	4	3400	15.66	1205
Retort, B. R. & P. 13		900° C.	4	3400	14.78	1137
Beehive, B. R. & P. 25		900° C.	4	3500	29.0	1160
Retort, B. R. & P. 25		900° C.	4	3500	24.0	960

A trial of 1000 tons of retort coke, made from Connellsville coal, coked in the Semet-Solvay ovens at Syracuse, was made at the Buffalo blast-furnace in the summer of 1895, and was reported upon by John Fulton, M. E. This test showed that as good results could be obtained with this coke as with the best standard Connellsville coke.

The blast-furnace at Dunbar, Penna., has used 160 tons of retort or by-product coke per day for the past three years; the furnace at Sharon, Penna., 80 tons; and for the past year the Ensley furnaces have been consuming 360 tons, and an oven plant at Wheeling has been furnishing 180 tons to furnaces in

that locality. It will thus be seen that the successful substitution of retort coke for beehive coke in the blast-furnace is no longer an experiment.

As a foundry coke, that made at Syracuse in the Semet-Solvay ovens is much sought after by the foundrymen, who are willing to pay twenty-five cents more per ton for the retort coke than for the beehive coke.

Foundry coke made in by-product ovens in England sells for two to three shillings more per ton than coke made from the same coal in beehive ovens by the same firm.

A test in a Pittsburg foundry of by-product coke, made from Pittsburg coal, showed that it did over twenty-five per cent. more work than the best beehive Connellsville coke.

RETORT OVENS LESSEN THE IMPURITIES IN COKE.

The theoretical yield, when applied to coke, signifies the coke obtained from 100 of coal by expelling the volatile matter and not permitting the combustion of any of the fixed carbon.

In beehive ovens, the yield of coke is from five to twenty per cent. less than the theoretical yield; in the Semet-Solvay retort ovens, we find in the large number of trials we have made on different coals, that the yield is greater than the theoretical by five to ten per cent., according to the coal under consideration. This is due to the fact that by the beehive method, much of the fixed carbon is burned, whereas, by the retort method, no fixed carbon is consumed because there is no admittance of air, and through the breaking-down of the gases much carbon is precipitated in and upon the coke.

The following figures illustrate by actual results obtained, the difference between coking in beehive and retort ovens. The importance of this increase of yield from a commercial as well as from a chemical standpoint is perfectly evident.

Kind of coal	Syracuse. Buffalo, Rochester and Pittsburg.	Dunbar. Connell- ville.	Sharon. Washing- ton.	Ensley. Alabama. Connell- ville.	Wheeling. Connell- ville.	Total.
Weight of coal coked per day (tons)	112	224	112	540	270	1258
Per cent. yield of coke per day.....	72	73	72	73	73	
Weight of coke per day (tons).....	80.6	163.5	80.6	394.2	197.2	916
Per cent. yield of coke in beehive oven from same coal..	65	66	65	60	66	
Weight of coke from beehive oven....	72.8	147.8	72.8	324	178.2	795.6
Per cent. increase in the yield of retort oven over beehive oven.....	10.7	10.6	10.7	21.6	10.6	

Further trials on well-known coals give the following results :

	Beehive. Per cent.	Retort oven. Per cent.	Gain. Per cent.
Pocahontas	62	83	33
Morris Run.....	60	80	33

It will thus be seen that the retort ovens actually lessen the percentage of sulphur, phosphorus, and ash impurities of the coke, by increasing the fixed carbon.

The sulphur in coal is present in three forms, as pyrites (FeS_2), or it is combined with carbon as a hydrocarbon, or it is present as calcium sulphate.

In the retort coke oven the organic sulphide is expelled and one-half of the sulphur of the pyrites, while the calcium sulphate remains unchanged. The sulphur remaining in the coke is almost invariably lower in percentage than in the coal.

The following are tests of sulphur in various coals coked in the ovens at Syracuse, and the sulphur in the coke made from these coals, also the volatile matter in the coals.

	PER CENT.								
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Sulphur in coal....	1.95	0.73	1.62	0.67	1.25	0.99	2.8	3.8	1.7
Sulphur in coke....	1.75	0.68	1.44	0.66	0.94	0.90	2.7	2.7	1.5
Vol. matter in coal.	38.2	23.7	27.3	25.4	31.8	37.8	40.1	40.4	29.6
Sulphur in coke supposing none evolved in coking	3.155	0.956	2.228	0.898	1.832	1.594	4.675	6.377	2.414
Per cent. sulphur removed	44.32	28.95	35.36	26.53	48.67	43.54	42.25	57.66	37.85

VOLATILE MATTER IN RETORT COKE.

The volatile matter in retort coke is quite as low and sometimes lower than in beehive coke. In passing it may be stated that the customary method of determining the volatile matter in coke, as described by Blair, gives results which are slightly too high, due to combustion of some of the fixed carbon. To completely prevent oxidation of the carbon on heating over a blast-lamp for three and one-half minutes, a stream of hydrogen or nitrogen is gently passed over the coke in the crucible, thus keeping the coke in an atmosphere of an inert gas during the heating; by this method a coke will show a volatile of 1.25 per cent., whereas, by the customary method, 2.25 per cent. volatile would have been shown.

Fig. 4 is a sketch of the apparatus used for determining the volatile matter in coke. It consists of a small platinum crucible with a cover tightly fitting the top of the crucible on the inside; through the cover is an inlet tube passing well down into the crucible, and an outlet tube on the cover. About ten grams of

fine coke are placed in the crucible, the cover put on, and a gentle stream of hydrogen or nitrogen, about two bubbles a second,

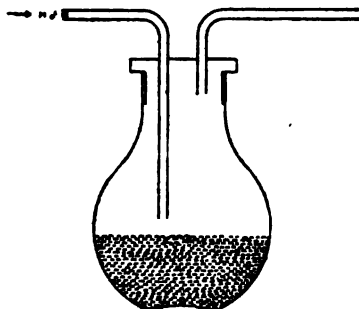


Fig. 4.

as indicated by a small bottle of water through which the gas passes, replaces the air and fills the crucible with the inert gas. The blast-lamp is then placed under the crucible and the coke heated for three and one-half minutes.

BY-PRODUCTS.

The by-products obtained from the distillation of coal in retort coke ovens are tar, ammonia, and gas, and from the gas may be recovered benzene and cyanides; all the by-products vary in quality and quantity with the composition of the coal, and are also affected more or less by the temperature to which the oven is heated. Generally speaking the quantity of tar and ammonia obtained is in direct proportion to the percentage of volatile matter in the coal. One containing seventeen per cent. volatile matter will yield 13½ lbs. of ammonia, figured as sulphate, and 30 lbs. of tar, whereas one containing thirty-seven per cent. volatile matter will yield 27 lbs. of ammonium sulphate, and 110 lbs. of tar. We are not referring now to the western coals, known as dry coals, which are devoid of bitumen and coke with great difficulty and yield a small amount of by-products, but to the coals found in the bituminous, or semibituminous fields of Pennsylvania, Virginia, West Virginia, Tennessee, Alabama, or Nova Scotia.

From the large number of ultimate analyses which we have made of coals experimented upon in ovens, we find that coals having the highest percentage of hydrogen over and above that necessary to combine with the oxygen in the coal, are the ones which make the best coke, and produce the greatest quantity of by-products; in other words, a coal containing a high percentage of oxygen will not produce good coke, nor will it produce much tar and ammonia. If the analysis shows water of consti-

tution five to ten per cent. indicating the character of a lignite, the yield of by-products will be small and the coke of poor quality ; or having at hand the proximate analysis of a coal found in any of the above-mentioned localities, one may judge very closely the yield of by-products per 2000 lbs. of coal by referring to the following chart. A line is also given showing the yield of coke to

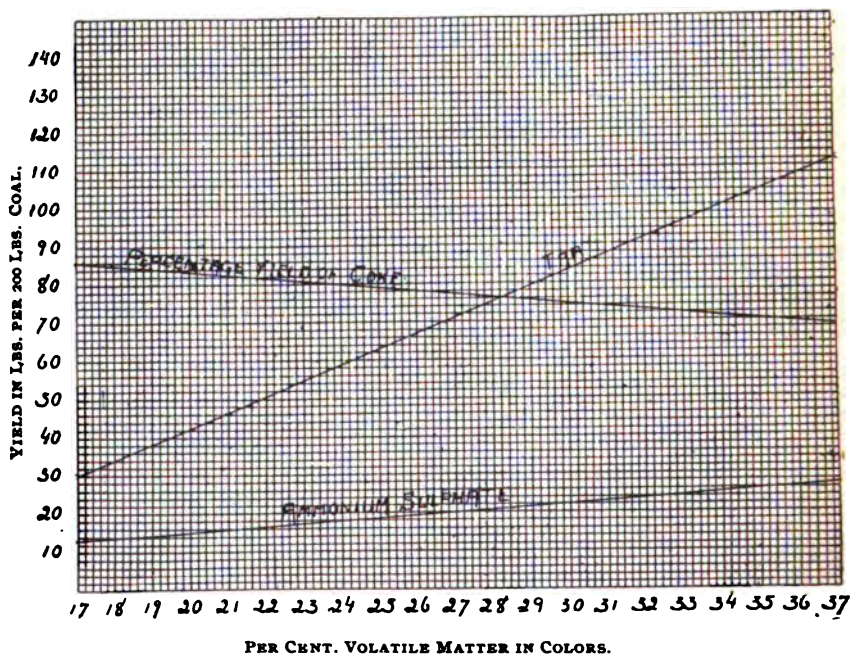


Fig. 5.—Chart showing lbs. of tar, ammonium sulphate per 2000 lbs. coal and percentage yield of coke for coals varying from seventeen per cent. to thirty-seven per cent. volatile matter.

be obtained. The higher the volatile matter the greater will be the increase in yield of coke over and above the theoretical. On this chart the increase in yield over the theoretical for a coal containing seventeen per cent. volatile is four per cent. ; for one containing thirty-seven per cent. it is eight per cent.

AMMONIA.

Weak liquor is converted to crude gas liquor, aqua ammonia, and sulphate.

While ammonia is formed from the organic nitrogen of the coal and while it is true that those coals highest in nitrogen also produce the most ammonia, still the amount of hydrogen present

in the coal over and above that necessary to combine with the oxygen of the coal, has an important influence in the yield of ammonia.

Coking coals do not vary greatly in nitrogen, from 1.30 to 1.60 per cent., whereas the yield of ammonia from coals containing these two percentages of nitrogen is 13½ and 27 lbs. ammonium sulphate respectively. It will thus be seen that the yield of ammonia is not exactly in proportion to the content of nitrogen in the coal. It will also be noted that this yield is a comparatively small percentage of the theoretical yield of ammonia from the nitrogen contained.

A coal of 1.30 per cent. nitrogen has a theoretical yield of 122.5 lbs. ammonium sulphate.

A coal of 1.60 per cent. nitrogen has a theoretical yield of 150.8 lbs. ammonium sulphate.

Thus in the first case eleven per cent. of the nitrogen is recovered as ammonia, and in the second case eighteen per cent. is obtained as ammonia.

William Foster' accounts for the nitrogen in coal when distilled in a gas retort as follows :

	Per cent.
Nitrogen of coal evolved as ammonia (NH ₃)	14.50
" " " " cyanogen	1.56
" present in gas as elementary nitrogen	35.26
" remaining in the coke	48.68

The addition of two per cent. of lime will increase the yield of ammonia ten per cent. This, however, could be done only with coals very low in ash.

The amount of nitrogen left in the coke varies greatly for the different coals. Many coals having very low nitrogen show the highest percentages of nitrogen in the coke. The following figures for nitrogen in coals and coke from them illustrates this point :

	I. Per cent.	II. Per cent.	IV. Per cent.	V. Per cent.
Nitrogen in coal	1.52	1.60	1.39	1.30
Nitrogen in coke	0.553	0.354	0.749	0.53
Volatile matter in coal	36.46	31.88	23.72	21.99
Nitrogen in coke if none evolved in coking ..	2.392	2.349	1.822	1.663
Nitrogen evolved as NH ₃ , CN and elementary nitrogen	76.88	84.51	58.88	68.13
Nitrogen of the coal recovered as NH ₃	19.26	13.88	15.02	11.43
Evolved nitrogen, recovered as NH ₃	25.02	16.39	25.51	16.78
Ammonia, figured as sulphate, recovered per 2000 lbs. coal (pounds)	25.36	20.93	19.67	14.00

To determine at what stage of the coking process the ammonia is expelled from an oven, a measured volume of gas was drawn through acid at different intervals and it was found that ammonia was evolved at the following rate. Eight samples of gas were tested during the twenty-four hours of coking.

RATE OF EVOLUTION OF AMMONIA PER 2000 LBS. COAL.

	Lbs.
At the end of 1 hour.....	16.2
4 hours.....	21.1
7 "	19.8
10 "	22.5
13 "	17.5
16 "	13.9
19 "	8.5
22 "	1.7

The ammonia is collected partly in the hydraulic main, partly in the condenser, and the last traces are removed from the gas in the scrubber. The liquor collected from these places is of course very weak and must be concentrated by distillation with lime to free the fixed ammonia. The weak liquors contain ammonia in the fixed and free state and include the carbonate, sulphate, sulphide, and chloride of ammonium. The weak liquors are of the following composition :

	Grams per liter.	
	Free ammonia.	Fixed ammonia.
Hydraulic main.....	1.18	7.14
Condenser.....	8.2	2.1
Scrubber.....	10.5	0.9

By distillation and condensation a crude ammonia liquor of seventeen per cent. to twenty per cent. ammonia is obtained. The sulphur and carbon dioxide combined with the ammonia in the weak liquor, reappear in the strong liquor. The composition of this liquor is:

Ammonia	17 to 20 per cent.
Carbon dioxide.....	75 to 80 grams per liter.
Hydrogen sulphide.....	30 to 35 " "

The quantity of ammonium sulphide, of course, depends upon the amount of the sulphur in the coal. There is always carbon dioxide in the gas from the oven in excess of the ammonia, hence a large amount of ammonium carbonate is necessarily formed. The principal other impurity in the crude concentrated liquor is ammonium cyanide, often present in such quantities as to make it profitable to recover it as potassium ferrocyanide; the greater part of the cyanogen, however, passes away in the gas, and after passing the scrubber may be treated for its removal.

Instead of making the crude yellow gas liquor of commerce, as above described, the process of distillation may be so carried on as to remove the carbon dioxide and hydrogen sulphide, and a product formed which is perfectly colorless, containing twenty-nine per cent. ammonia, and known in the trade as aqua ammonia. The following table shows the relation of °Bé to per cent. ammonia in aqua ammonia :

AQUA AMMONIA.

Table adopted by National Ammonia Co.

Table by G. Gerhardt.

Specific Gravity, 60° Fah.	Degrees Baumé (Gerhardt).	Per cent. ammonia.	Factor.
1.0000	10	0.0	0.0000
0.9930	11	1.6	0.055168
0.9864	12	3.3	0.1138
0.9793	13	5.05	0.1741
0.9726	14	6.80	0.23445
0.9660	15	8.33	0.2872
0.9594	16	10.17	0.35066
0.9530	17	11.88	0.4096
0.9467	18	13.88	0.47858
0.9400	19	15.63	0.5389
0.9342	20	16.42	0.6006
0.9281	21	19.25	0.6637
0.9221	22	21.12	0.7282
0.9191	22.5	22.07	0.76097
0.9161	23	23.03	0.7941
0.9132	23.5	24.00	0.8175
0.9102	24	25.00	0.8620
0.9073	24.5	25.98	0.8958
0.9045	25	26.98	0.9303
0.9016	25.5	27.60	0.9516
0.8986	26	29.00	1.0000
0.8959	26.5	29.69	1.0237

To meet the demands of manufacturers of fertilizers, the gases from the distiller may be absorbed in 60° sulphuric acid contained in a lead-lined tank called a saturator, and crystals of ammonium sulphate obtained. The color of the crude commercial ammonium sulphate is usually gray, but is sometimes blue. Blue sulphate brings a much lower price than the gray. The blue color is due to the presence of Prussian blue formed from the ammonium cyanide in the weak liquor. By special treatment of this liquor before distillation a gray sulphate may invariably be obtained.

TAR.

As previously stated the amount of tar recovered varies from 30 to 110 lbs. per 2,000 lbs. coal, according to the composition of coal. The tar, like the ammonia, is separated from the gas in the hydraulic main, condenser, and scrubber.

The quality of tar from retort coke ovens varies greatly ; the

quantity as before stated depends upon the composition of the coal, the temperature of the ovens, and the pressure of the gas between the oven and the hydraulic main; the same may be said to be true of the quality of the tar. It is also true that coals, identical as far as the proximate analysis is concerned, sometimes produce tars which are widely different in composition. It is difficult to say why this should be so; it is probably due to slightly different conditions of operation, and partly due to a difference in the coal which is not shown in the proximate analysis. The relation of the carbon to the hydrogen in the volatile matter is different. A coal in which the hydrogen is a large percentage of the carbon in the volatile matter, produces a tar containing much naphthalene; and we find on the other hand that the amount of naphthalene in a tar from a coal very low in hydrogen is very small. To illustrate: In one of our plants the tar obtained is so highly charged with naphthalene that on distillation the very first distillate up to 100° C. solidifies, whereas, in another plant, the tar obtained shows only traces of naphthalene, though the coals used are almost identical, judging from the proximate analysis. Analyses of these two coals and the tar obtained are:

ANALYSES OF COALS.

	A. Per cent.	B. Per cent.
Volatile matter.....	34.20	32.68
Fixed carbon	57.15	59.40
Ash	8.65	7.92
Sulphur	0.93	1.19

ANALYSES OF TAR.

	A. 1.163	B. 1.203	I. 1.205	II. 1.231
	Per cent.	Per cent.	Per cent.	Per cent.
Water.....	2.40	2.70	1.40	1.10
Light oil.....	4.60	2.03	3.12	1.63
Creosoting oil.....	1.26	0.50	0.29	0.34
Dead oil.....	22.81	16.40	25.09	19.23
Naphthalene	6.0	trace	0.20	1.72
Anthracene.....	0.6	"	0.19	0.24
Soft pitch	68.80	70.50	67.40	74.14

Tars A and B show what differences may exist in tars made from coals very similar in proximate analysis. I and II represent two tars from gas houses, which also vary greatly, but as a usual thing are found to be of a much higher specific gravity and to contain less light oils, making them inferior for the manufacture of benzene, and the dipping of paper for tarred paper.

The analyses of tar given above were made by a method which gives results that enable a tar distiller to judge of what the com-

mercial value of the tar is. A tar distiller wants to know how much light oil, naphthalene, dead oil, and soft pitch a tar will give. There is as yet no market for anthracene in this country. Most analyses given in books show too low a percentage of pitch. There is practically no market for hard pitch. To produce a salable pitch distillation must be stopped at 355° to 360° C. The method of analysis used for the determination of the commercial value of tar is as follows:

In the first place no test should be made on a quantity less than a gallon.

Method.—Weigh out ten lbs. tar in a measured cylinder, and in this way determine the specific gravity of the tar.

The thermometer in the distillation of tar should be placed one-half inch above the surface of the liquid.

Keep the tar at a temperature of 50° C. for twelve hours. Water comes to the surface, which is to be removed and measured, and is to be reckoned in the analysis of the tar.

Put the balance of the tar into a copper still, of two gallons capacity, and begin the distillation very slowly at first, the distillate coming one drop per second. Have a beaker of water, into which place a drop of the distillate when the light oil is coming over, to indicate the point when the light oil changes into heavy oil and sinks in water. The distillate is then turned into another receiver, and the light oil and water in the first receiver carefully measured. The distillation is then continued up to about 360° C., or to such a point as produces a roofing pitch in the still, which may be determined by taking a sample from the still, putting in water, and testing the cooled sample.

If it has cohesive properties, that is, if it makes a gum, it is of good quality. If it is brittle, the distillation has been carried too far, and the residue in the still will be hard pitch, which is unsalable.

The temperature of the condenser should be kept at 75° C. during this distillation. The distillate should stand for some twelve hours at a temperature of about 60° F. The roofing pitch in the still, after cooling, should be removed by unsealing the top, which is bolted, and turning the still upside down; upon gently heating the bottom of the still the pitch will drop out in one large cake. This is then weighed and constitutes the percentage of roofing pitch in the tar.

The distillate contains the creosote oil, dead oil, naphthalene, and a portion of the anthracene, it being necessary to have held in the pitch some of the anthracene to produce a pitch of the right quality for roofing purposes. The distillate with its crystallized naphthalene and anthracene is transferred to a Canton flannel cloth and compressed to remove the liquor as much as

possible by hand; then it is placed between one-quarter inch iron plates and put into a vise and pressed for about one-half day, every little while tightening the vise; this pressed cake represents the crude naphthalene and crude anthracene over and above the amount remaining dissolved in the dead oil. The liquor resulting upon compressing and removing the naphthalene and anthracene contains the creosoting and dead oil. This oil is placed in a small copper still of about one liter capacity. The distillate resulting up to 200° C. is the creosoting oil; the balance in the still is dead oil.

To separate the anthracene from the naphthalene melt up the material from which the oil has been pressed, put in a still and distil up to 280° C. (This distillate is crude naphthalene.) Now save the fraction distilling from 280° C. to dryness (this is anthracene mixed with a little anthracene oil.) Press this as with the larger amount before, and the solid matter remaining in the cloth is the crude anthracene. This subtracted from the total will give the crude naphthalene also.

PRACTICAL TEST FOR ROOFING PITCH.

The practical test for roofing pitch is to take a sample, place it in the mouth and chew it, and if there is a sufficient amount of cohesion to produce a gum, the roofing pitch is of good quality. This is a very crude test, but is the one used in the tar distillation works.

GAS.

A portion for heating ovens; the surplus for illumination, fuel purposes, or for power in gas engines.

The total volume of gas evolved from a coal is of course directly proportionate to its percentage of volatile matter and the heat to which it is exposed. This holds true of the gas from a retort coke oven, provided leaky flues do not admit air to burn the gas in the oven, or under conditions of excessive pressure gas is not driven into the flues and there burned. But in well-constructed and well-regulated ovens this need never occur.

The total volume of gas from a coal containing thirty-three to thirty-four per cent. volatile matter is about 10,400 cubic feet per long ton, or 9,280 cubic feet per 2000 lbs.; from a coal of twenty per cent. volatile matter, about 7000 cubic feet per long ton, or 6250 cubic feet per 2000 pounds.

The quantity of gas necessary to be returned to the oven for heating is from fifty to fifty-five per cent. if the coal is thirty-two to thirty-four per cent. volatile. Less gas is required to coke coals of low volatile composition. Thus Pocahontas coal containing nineteen per cent. volatile matter requires only two-thirds as much gas for coking as Connellsville coal, which contains thirty-two per cent. volatile.

I give below the results obtained from the coking of a coal in an isolated oven; analyses of this gas taken after passing the purifying box were made hourly during the period of coking, which was twenty-four hours.

Photometric readings were made every five minutes, the tests averaged and recorded for every hour calculated for a consumption of five feet per hour at 60° F. and thirty inches mercury, each candle-power being equal to 120 grams spermaceti per hour. The photometer used was a sixty-inch bar photometer.

The analysis of the coal used in this test was as follows:

	Per cent.
Volatile	35.71
Fixed carbon	59.36
Ash	4.93
Sulphur	2.4
Nitrogen	1.52
Cubic feet.	
Total volume of gas from 9,400 lbs. coal	43,747
" " " " 2,000 " "	9,280
" " " " 2,240 " "	10,400

Using this same coal in the entire twenty-five ovens for forty-eight hours and turning the excess or surplus gas into holders, we found that this excess gas amounted to 44.5 per cent. of the total gas; in other words:

Total gas	9,280 cubic feet per 2000 lbs. coal.
Percentage gas for coking	55.5 per cent.
Volume gas for coking	5,150 cu. ft.
Percentage of surplus gas	45.5 per cent.
Volume of surplus gas	4,130 cu. ft.

These figures represent accurately the distribution of the gas when making blast-furnace coke. If only domestic coke is to be the product, fifteen to twenty per cent. less gas will be required for the coking process.

The following are the records of gas analyses made hourly, and from a perusal of them we see that the methane at the beginning is very high, forty-six per cent., and that it soon falls to forty per cent. and remains at this figure for about twelve hours, and then begins to fall off until, at the discharge, the gas contains only 10.2 per cent. The hydrogen on the other hand starts in at 28.9 and is ever increasing, until at the end it has reached 77.0 per cent. The illuminants (olefines) are highest, 6.8 per cent., in the beginning and gradually diminish, until after sixteen hours they are practically nil. The carbon monoxide, nine per cent. in the first test, gradually decreases until in the last test four per cent. is found.

The high nitrogen in the early tests is due to an excessive suction on the oven:

REVIEW.

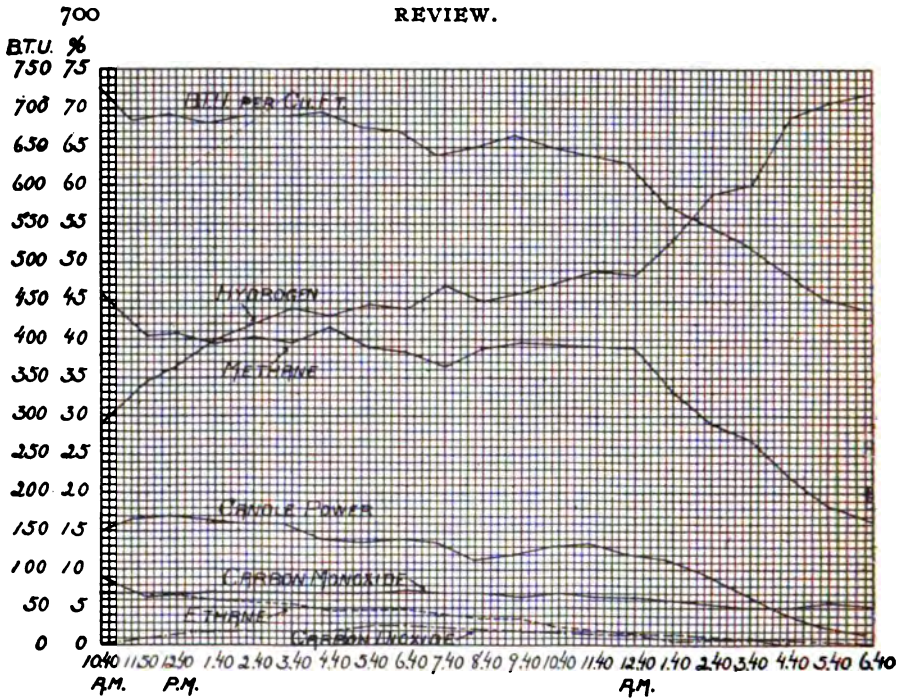


Fig. 6.—Hourly record of analyses, candle power and B. T. U. per cu. ft. of gas from one coke oven.

Time.	Carbon dioxide.	Ethyl-ene.	Oxygen.	Carbon monoxide.	Methane.	Hydrogen.	Nitrogen.
10.40 A.M.	0.0	6.8	1.0	9.0	46.0	28.9	8.3
11.50	1.2	6.8	1.0	6.4	40.5	34.3	9.8
12.40 P.M.	1.6	6.7	0.7	6.7	40.8	36.7	6.8
1.40	2.0	6.0	0.6	6.9	39.5	40.2	4.8
2.40	2.0	5.6	0.4	6.8	40.3	42.1	2.8
3.40	2.0	5.5	0.3	6.8	39.6	44.0	1.8
4.40	2.0	4.8	0.4	7.0	41.5	43.3	1.0
5.40	2.5	4.7	0.5	7.0	39.2	44.7	1.4
6.40	2.5	4.8	0.8	7.2	38.8	43.9	2.0
7.40	2.3	4.2	0.5	6.9	36.4	47.2	2.5
8.40	2.3	3.6	0.4	6.8	38.9	45.2	2.8
9.40	2.1	3.7	0.3	6.6	39.7	46.0	1.6
10.40	2.1	2.7	0.3	7.0	39.3	47.5	1.1
11.40	1.5	2.2	0.4	6.6	39.2	48.9	1.2
12.40 A.M.	1.4	1.7	0.8	6.5	38.8	48.5	2.3
1.40	0.7	1.4	0.4	5.9	33.1	52.9	5.6
2.40	0.8	1.0	0.3	5.4	28.9	59.2	4.4
3.40	0.5	0.8	0.2	5.0	26.9	60.2	6.4
4.40	0.0	0.0	0.3	4.9	22.3	68.9	3.4
5.40	0.2	0.0	0.3	5.5	18.3	70.8	4.9
6.40	0.0	0.0	0.4	5.3	16.4	72.1	5.8
7.40	0.2	0.0	0.2	4.3	12.9	73.5	8.9
8.40	0.0	0.0	0.4	4.0	10.8	75.0	9.8
9.40	0.0	0.0	0.2	4.0	10.2	77.0	8.8

The following table shows the calorific value of the gas from hour to hour and also the candle-power :

Time.	Average candle-power for each hour.	Calories per cubic meter.	Calories per cubic foot.	B. T. U. per cubic foot.
10-11 A.M.	15.1	6539	185	734
11-12	16.7	6104	173	686
12-1 P.M.	17.2	6201	175	694
1-2	16.5	6088	172	682
2-3	15.8	6158	174	690
3-4	16.0	6135	174	690
4-5	13.9	6195	175	694
5-6	13.3	6004	170	674
6-7	13.9	5963	169	670
7-8	13.4	5739	162	642
8-9	11.3	5821	164	650
9-10	11.9	5931	168	666
10-11	12.9	5802	164	650
11-12	13.5	5748	162	642
12-1 A.M.	12.2	5621	159	631
1-2	11.4	5151	145	575
2-3	9.3	4871	138	547
3-4	6.8	4669	132	523
4-5	4.2	4377	124	492
5-6	2.6	4074	115	456
6-7	1.6	3927	111	440
7-8	0.0	3607	102	404
8-9	0.0	3439	97	384
9-10	0.0	3235	91	361

From a study of these figures it will be seen that as an illuminating gas it is not of much value after ten hours. In calorific value, however, it has diminished only slightly.

From the following table it will be seen that the volume of gas expelled per hour remains pretty nearly constant for seventeen hours and then falls off rapidly :

1. Time.
2. Cubic feet of gas expelled from the oven per hour.
3. Average of the several readings of the candle-power during each hour.
4. Total cubic feet of gas expelled from hour to hour.
5. The percentage of total cubic feet of gas expelled at the end of each hour.
6. Average candle-power of the total gas.

1.	2.	3.	4.	5.	6.
10-11	2032	15.1
11-12	2272	16.7	4304	9.8	15.9
12-1	2075	17.2	6379	14.5	16.3
1-2	1934	16.5	8313	19.0	16.4
2-3	1974	15.8	10287	23.5	16.2
3-4	2068	16.0	12355	28.2	16.2
4-5	1880	13.9	14235	32.5	15.9
5-6	1880	13.3	16115	36.8	15.6
6-7	1880	13.9	17995	41.1	15.4

1.	2.	3.	4.	5.	6.
7-8	1974	13.4	19969	45.6	15.2
8-9	2068	11.3	22037	50.3	14.8
9-10	2162	11.9	14199	55.3	14.6
10-11	2256	12.9	26455	69.47	14.4
11-12	2162	13.5	28617	65.41	14.4
12-1	2068	12.2	30685	70.14	14.2
1-2	2350	11.4	33035	75.51	14.0
2-3	2162	9.3	35197	80.45	13.8
3-4	2350	6.8	37547	85.82	13.4
4-5	1598	4.2	39145	89.48	12.9
5-6	1410	2.6	40555	92.70	12.4
6-7	1034	1.6	41589	95.06	11.9
7-8	940	0.0	42529	97.21	11.3
8-9	889	0.0	43418	99.24	10.8
9-10	339	0.0	43747	100.00	10.4

In the above tables we have the means of determining the most advantageous disposition to make of the gas from a plant of retort coke ovens.

First, the first forty-five per cent. of the gas expelled may be received in a holder and used without enrichment, as is done with the gas from the ten Semet-Solvay ovens at Halifax. These ovens were erected to take the place of others of a different type which were a failure. Or, second, the entire gas from the ovens may be enriched and brought from 10.4 to 16 or 17 candle-power and used for illuminating purposes; or third, the entire gas may be pumped to street mains for domestic fuel supply, without enrichment.

In either of the two last cases producer gas would be substituted for the coke oven gas for heating the ovens. This is perfectly practical, and profitable, if there is a demand for all the coke oven gas.

The following table shows the composition of the surplus gas, and of the balance of the gas which would ordinarily be used for heating the ovens; Fig. 5 also represents graphically the analyses of gas, etc.

ANALYSES.

	Carbon dioxide.	Illuminants.	Oxy-gen.	Carbon monoxide.	Hydro-gen.	Meth-ane.	Nitro-gen.
Surplus gas	1.8	5.5	0.6	6.4	40.5	40.2	4.9
Heating gas	0.8	1.2	0.3	5.6	60.4	26.8	4.9
Average	1.3	3.4	0.45	6.0	50.45	33.5	4.9

HEAT UNITS.

	Volume in per cent.	Volume per 1000 lbs. Cu. ft.	Volume per long ton. Cu. ft.	Calorific power.		
				B. T. U.	Calories per cubic-meter.	Candle-power.
Surplus gas	45.5	4130	4732	685	6112	15.2
Heating gas	55.5	5150	5668	532	4734	8.3
Average and total..	100.0	9280	10400	608.5	5423	11.7

To compare with retort coke oven gas in composition and fuel value are taken figures of retort gas, given by C. D. Jenkins, State gas inspector of Massachusetts, in his report of 1896. For analyses of natural gas, average of figures given by Prof. F. C. Phillips, *Am. Phil. Soc.*, 17, have been adopted.

	Natural gas. Per cent.	Illuminating gas. Per cent.	Coke Oven gas. Per cent.	Water gas. Per cent.	Producer gas. Per cent.
Carbon dioxide.....	0.48	1.75	1.3	0.14	4.5
Illuminants	0.0	4.88	3.4	...	0.0
Oxygen.....	0.0	...	0.45	0.13	0.6
Carbon monoxide	0.0	6.82	6.0	37.97	25.5
Methane.....	92.47	33.90	33.5	7.65	1.0
Hydrogen.....	0.0	46.15	50.45	49.32	12.0
Nitrogen.....	7.05	6.50	4.9	4.79	56.4
B. T. U. per cu. ft.	984	623	608.5	381	138

From the above figures it will be seen that coke oven gas is greatly superior for heating purposes to producer and water gas, and only slightly inferior to illuminating gas. Of course, natural gas, composed so largely of methane, yields a much greater number of calories.

BENZENE OBTAINED FROM THE TAR AND FROM THE GAS.

Benzene and the other products of this series are evolved during the early stages of the coking process. They are condensed and appear in the lighter portions of the tar, or become fixed in the gas, and may be removed only by pressure and low temperature, or by dissolving in oils. By far the greater proportion of the benzene from a ton of coal is recovered from the gas, only about ten per cent. from tar. As the illuminating quality of a coke oven gas is largely due to the benzene (C_6H_6) contained, it is evident that the removal may greatly deteriorate its value for lighting purposes, while the heating value of the gas is only slightly affected. The first product obtained after treating the absorbent containing the benzene is known in the trade as "light oil." The light oil obtained from the gas is six and six-tenths lbs. to eight and five-tenths lbs. per long ton of coal, and varies with the percentage of volatile matter in the coal.

The light oil contains from fifty-eight to sixty-three per cent. of benzene, divided thus :

	Per cent.
Ninety per cent. benzene.....	57
Fifty per cent. benzene.....	2
Solvent naphtha	4

Distillation of this light oil gives a product distilling as follows :

Density at 15° C.....	0.92
First drop.....	81.5° C
At 100° C.....	50.0 per cent. distilled
At 125° C.....	66.0 " " "
At 150° C.....	71.0 " " "
At 170° C.....	74.0 " " "

From the distillation of this product the ninety per cent. and fifty per cent. benzene and solvent naphtha of commerce are obtained. The analyses of these products are as follows:

NINETY PER CENT. BENZENE.

Density	0.89
First drop at	81.5° C.
	Per cent.
At 85° C.....	40
At 90° C.....	77
At 95° C.....	86
At 100° C.....	91-92

FIFTY PER CENT. BENZENE.

Density	0.884
First drop at	87° C.
	Per cent.
At 90° C.....	7.5
At 100° C.....	52
At 120° C.....	90-91.5

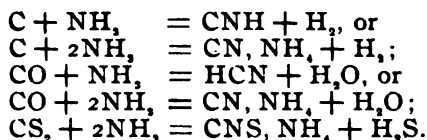
SOLVENT NAPHTHA.

Density	0.88
First drop at	116° C.
	Per cent.
At 120° C.....	6
At 160° C.....	99-91.5

CYANIDES.

As in the case with ammonia, cyanogen is evolved in greatest quantity about the eighth to the tenth hour of coking.

The formation of cyanogen in illuminating gas has been accounted for by Kuhlman through the action of ammonia on carbon, carbon monoxide, and carbon disulphide in the following reactions:



In the retort coke ovens we have similar conditions to the gas retort. It is, however, different in that the charge of coal is much greater, and the temperature is not so high; the quantity

of cyanogen obtained therefore is not so great from the retort coke oven, for high temperature is conducive to high yield. We find on testing the gas from the oven before entering the hydraulic main, that both thiocyanate and cyanides of ammonia are present; but that on testing the liquor from the hydraulic main, we do not find any ammonium cyanide or ammonium ferrocyanide. Even though the temperature of this liquor in the main is low, and one would expect the ammonium cyanide to remain in solution, we find that in the struggle for ascendancy, carbonic acid and other acids expel the cyanogen, and it passes on with the gas.

In the examination of the ammonia liquor from the condenser, we find only a small amount of thiocyanate present, but a comparatively large amount of ammonium ferrocyanide. The only explanation to offer for this is that ferrous sulphide is formed by contact of the hydrogen sulphide with the very large expanse of metal in the condensers. This ferrous sulphide in an atmosphere of ammonia as an alkali forms with hydrocyanic acid, ammonium ferrocyanide. In the scrubber we find thiocyanate, but no ammonium cyanide or ferrocyanide.

Thiocyanate found in the different liquors is:

In hydraulic main....	1.501	grams per liter ammonium thiocyanate.
Condenser.....	0.0912	
Washer	0.0058	

The gas leaving the scrubber contains the cyanogen in the form of hydrocyanic acid, and when hydrocyanic acid is recovered by the usual method, *i. e.*, passing the gas through an alkaline ferrous carbonate or sulphide absorbing solution, by which potassium ferrocyanide is formed, we find a considerable amount of sodium thiocyanate in the solution. In fact, our tests show that in this absorbing solution the cyanogen is divided as follows:

	Per cent.
Cyanogen as $K_4Fe(CN)_6 \cdot 3H_2O$	92.61
" KCNS.....	7.39

The cyanogen recoverable from coke oven gas, figured as potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) amounts from 1.25 to 1.50 lbs. per 2000 lbs. of coal.

The amount of cyanogen recovered in weak ammonia liquors, as ammonium thiocyanate and ferrocyanide, if added to the above yield, would increase the yield of potassium ferrocyanide one-tenth lb. per 2000 lbs. of coal.

J. D. PENNOCK.

NOTE.

*The Occurrence of Vanadium, Chromium, and Titanium in Peats.*¹—Attention has been called by Dr. W. F. Hillebrand² to the comparatively wide-spread occurrence of vanadium in a large number of minerals and rocks. He states that "Hayes in 1875 reported its occurrence in a great variety of rocks and ores. Quoting from Thorpe's 'Dictionary of Chemistry,' 'it is said to be diffused with titanium through all primitive granite rocks (Dieulafait) and has been found by Deville in bauxite, rutile, and many other minerals, and by Bechi and others in the ashes of plants and in argillaceous limestones, schists, and sands....' It is further reported to comprise as V_2O_5 0.02–0.07 per cent. of many French clays, 0.02–0.03 per cent. of some basalts, 0.24 per cent. of a coal of unknown origin, and 0.45 per cent. of one from Peru, amounting to 38.5 per cent. and 38.0 per cent. of the ash, and noted respectively by Mourlot and Torricio y Meca."

Roussel³ states that a basalt with a content of 0.707–2.378 per cent. of titanium contained 0.006–0.023 per cent. of vanadium. Gladstone,⁴ however, states that it does not occur in the volcanic dust of Vesuvius. Terrèil⁵ found it in iron ores. Stolba⁶ also mentions its occurrence.

From the above the presence of vanadium could with reason be suspected in peat. In the hands of the writer were samples of peats from Hyde Swamps, one mile south of Pungo Lake near the Northern Junction of Beaufort and Hyde Counties, N. C. The approximate analysis of these peats gave :

Sample	Water.	Volatile matter.	Fixed carbon.	Ash.
Peat I.....	73.67	16.16	9.72	0.45
Peat II.....	71.58	17.42	10.31	0.69
Peat III.....	76.01	14.19	9.32	0.48

The water was determined by taking a cube measuring about eight cm. each way (from 700 to 800 grams) and bringing to a constant weight by heating for a number of hours not higher

¹ Read before the North Carolina Section at the midwinter meeting.

² *Am. J. Sci.*, 6, 209 (1898).

³ *Ber. d. chem. Ges.*, 6, 1417 b.

⁴ *Ibid.*, 5, 815 b.

⁵ *Ibid.*, 10, 731 a.

⁶ *Chem. Centrbl.* (1897), 121.

than 105° C. An analysis, approximate, of this dried peat gave the following results :

Sample.	Volatile matter.	Fixed carbon.	Ash.
Peat I.....	61.38	36.90	1.72
Peat II.....	61.35	36.20	2.45
Peat III.....	59.13	38.85	2.02

It was convenient to examine the ash of a large number of peats from this and other localities to ascertain the presence of titanium. We have found no statements regarding the presence of this element in these ashes, although such a surmise was logical. Neither does chemical literature, as far as we have been able to examine, give any mention of the occurrence of chromium in peats. Appended are the results of seeking for these elements in the samples mentioned above.

Sample.	Titanic oxide.	Chromium sesquioxide.	Vanadium pentoxide. Percentages in ash.
Peat I	0.490	0.0283	0.00107
Peat II	0.340	0.0343	0.0026
Peat III	0.491	0.0355	0.0031

In determining titanium the ash was decomposed according to the method of W. A. Noyes,¹ namely, by fusion with sodium fluoride and potassium pyrosulphate. The melt was brought into solution with Dunnington's² necessary precaution in mind ; *viz.*, having from five to ten per cent. of sulphuric acid present. Hydrogen dioxide was added according to Weller's³ well-known method and the titanium determined colorimetrically. All hydrofluoric acid was driven off in the fusion and the hydrogen dioxide was free from that acid as well. Hillebrand⁴ has shown the necessity for this.

Chromium⁵ and vanadium⁶ were estimated according to the latest method of Hillebrand. CHAS. BASKERVILLE.

UNIVERSITY OF NORTH CAROLINA.

¹ *J. Anal. Appl. Chem.*, 5, 39.

² *This Journal*, 13, 210.

³ *Ber. d. chem. Ges.*, 15, 2592.

⁴ *This Journal*, 17, 718; *Chem. News.*, 72, 158.

⁵ *This Journal*, 20, 454.

⁶ *Ibid.*, 20, 461; *Am. J. Sci.*, 6, 209.

NEW BOOKS.

VICTOR V. RICHTER'S ORGANIC CHEMISTRY OR CHEMISTRY OF THE CARBON COMPOUNDS, edited by PROF. R. ANSCHÜTZ. Authorized translation by EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania. Third American from the eighth German edition. VOL. I, CHEMISTRY OF THE ALIPHATIC SERIES. Philadelphia: P. Blakiston's Son & Co. 625 pp. Price, \$3.00.

There are at present three pretty clearly defined classes of works on organic chemistry: (1) elementary text-books, which aim to give a systematic account of the general principles of the science and of the more important typical compounds and their relations to each other; (2) larger text-books, containing large quantities of material necessarily omitted from books of the first class, —material which the student will find very useful to have always at hand on his study-table or at his laboratory desk, but most of which no student can ever master in all of its detail; and (3) hand-books, aiming to give a complete record of the facts of the science now known. The book before us is one of the best of the works of the second class. The work of revision, which is imperatively necessary at frequent intervals in this subject, has been ably executed by Professor Anschütz. The translation by Professor Smith is clear and very satisfactory. It is impossible to avoid some errors in proof-reading, of course, but such errors appear to be very infrequent.

The discussion of the general principles of nomenclature, on p. 57, is too short to be satisfactory, and the attitude assumed toward the proposals of the Geneva Commission is disappointing. Also the promise that "the more important suggestions of the commission will receive full consideration under the various classes of bodies" is not fulfilled in such a manner that a beginner is likely to get a clear idea of the Geneva nomenclature from the book.

The brief, clear, historical treatment of many topics is a very excellent feature and adds greatly to the value of the book.

W. A. NOYES.

TRAITÉ D'ANALYSE CHIMIQUE QUANTITATIVE PAR ELECTROLYSE. PAR J. RIBAN, Professeur Chargé du d'Analyse Chimique, etc., L'Université de Paris. Paris: Masson et Cie, 1899. vi + 304 pp.

This volume consists of four parts. The first part considers

certain elementary physical subjects, indispensable to those carrying out determinations in the electrolytic way, such as the laws relating to the electric current, apparatus for its measurement and for its control, as well as descriptions of various forms of apparatus used in electrochemical analysis. The subject-matter is presented in a clear, complete, and interesting form.

The second part deals with the electrolytic determination of the individual metals and non-metals. The author first mentions arsenic, which cannot be fully deposited electrolytically, and then gives a very extended account of the various suggestions which have been made for the estimation of antimony. Perhaps the order of presentation is of little moment, but experience has led the reviewer to the opinion that it is better to commence with simple acid solutions, *e.g.*, copper in nitric acid, and gradually advance to those examples, which from natural conditions are more difficult to handle. This portion of the book is very complete in its presentation of the methods of all persons who have labored in this field. Here and there names of authors appear incorrectly spelled, and attached sometimes to methods which did not originate with them. This, however, is immaterial, for the student of the volume is given a very exhaustive description of what has been achieved, and is left to ascertain for himself which methods are the most satisfactory for his purposes.

The separation of the metals constitutes the third section. The first example is that of antimony from tin in a solution of sodium sulphide. This is far from being an easy problem. The method is beset with difficulties which even the most experienced have had trouble to remove.¹ The numerous methods given for other separations have in nearly all instances proved entirely satisfactory.

In the fourth part the author gives very excellent and explicit directions for the analysis, in the electrolytic way, of many alloys and commercial products. For this he deserves the thanks of all interested in the extension of the methods which have been successfully worked out for two or three metals when present in the same solution. On page 275 the student is directed in analyzing cinnabar, to dissolve it in hydrobromic acid, and after neutralizing with caustic potash and adding an excess of

¹ See *Ztschr. angew. Chem.* (1897), Heft 10; *Ztschr. Elektrochemie*, 4, 245.

potassium cyanide to proceed with the determination of the mercury. Time would be saved and disturbing constituents be eliminated by simply digesting the mineral with sodium sulphide, in which it is soluble, and after the removal of the insoluble parts by filtration, proceeding as directed under the determination of mercury. It is a great pity that literature references are omitted from the entire text.

Tables, showing the E. M. F. of various batteries, factors for the calculation of certain electrolytic data, electrochemical equivalents, the intensity of current expressed in volumes of electrolytic gas with their equivalents in amperes, resistances of metals and alloys, etc., etc., conclude the book, which is well printed and illustrated. It deserves a prominent place in electrolytic literature.

EDGAR F. SMITH.

PHYSICAL CHEMISTRY FOR BEGINNERS. BY DR. CH. VAN DEVENTER.

With an Introduction by PROF. J. H. VAN'T HOFF. Authorized American edition from the German edition, translated by BERTRAM B. BOLTWOOD. New York: John Wiley and Sons. 1899. x + 156 pp. Price, \$1.50

THE ELEMENTS OF PHYSICAL CHEMISTRY. BY J. LIVINGSTON R. MORGAN, PH.D. New York: John Wiley and Sons. 1899. viii + 299 pp. Price, \$2.00.

The reviewer has already¹ called attention to the need of a text-book on physical chemistry presenting the main facts and theories of this important branch of the science in a form not demanding too much preparation in physics or mathematics on the part of the student, and he is much pleased to note the appearance of these two books which go far towards filling this need. With such books at hand there is no reason why instruction in physical chemistry should not be given in even our smaller universities and colleges. A knowledge of the rôle that ions play in the reactions of analytical chemistry throws such a flood of light on that subject that it ought to be acquired by the student at the same time he is practising analysis in the laboratory. Instead of deferring the study of physical or theoretical chemistry until after courses in qualitative and quantitative analysis have been completed, it should be taken up along with them. The danger of work in analytical chemistry degenera-

¹ See the review of Clarence L. Speyers' "Text-Book of Physical Chemistry," in this Journal, 20, 389 (1898).

ting into mere routine and the acquisition of manipulative dexterity would certainly be avoided in a large measure by so doing.

These two books are in many respects complementary to each other. Boltwood's book is the more elementary, containing much that is usually given in good courses in beginning chemistry. In it but little space is devoted to methods, experimental or theoretical, and the treatment is strictly non-mathematical. The general plan is to state carefully laws and principles and then to illustrate them by remarks, historical, critical, etc.

Morgan assumes that the student has a knowledge of the rudiments of calculus, and to a not inconsiderable extent gives the mathematical derivation of many laws. He also sketches in broad outlines the chief pieces of apparatus and modes of using them, that have proved of such great service in the development of physical chemistry.

While Boltwood hardly more than touches upon the subjects of electrochemistry and ionization, Morgan treats of them excellently and at length, the doctrine of ions appearing all through his book. On the other hand, Boltwood takes up in some detail photochemistry and the periodic law, which are barely mentioned by Morgan.

Errors of importance are scarcely to be found in either book. As to the translation, although the translator in "closely following the German text in nearly all cases" (p. vi.) has in places let the German idiom appear too glaringly, yet on the whole he has succeeded in attaining a commendable smoothness and clearness of language. The reviewer would, however, deprecate the use of the expression "heat toning," inasmuch as heat effect expresses the same thing in good English.

The two books as issuing from the same publishing house are very similar in their make-up, the typography, presswork and binding being practically the same. C. E. LINEBARGER.

THE MICROSCOPY OF DRINKING WATER. BY GEORGE CHANDLER WHIPPLE. Biologist and Director of Mount Prospect Laboratory, Brooklyn, N. Y. First edition. New York: John Wiley & Sons. 292 pp.

It may without doubt be safely assumed that there are few water analysts who would not concede the value of a carefully conducted and intelligently interpreted microscopical examina-

tion of the suspended matter and sediment often found in drinking water, and it is quite conceivable that the result of such an examination may be a determining factor in deciding the question of the fitness, or the contrary, of a water for drinking purposes. And, whilst it must be admitted that, in the majority of cases, chemistry alone is competent to enable an expert to decide upon the quality of a water, the fact that there are many occasions in which an appeal to the microscope may be of great value and importance, is a good *raison d'être* for such a work as this.

Following a brief but interesting historical survey of the study of the micro-organisms in water from the time of Hooke and Lieuwenhock, is a chapter on the object of the microscopical examination of water, and this by an excellent one on "Methods of Examination," which, while more elaborate than the majority of chemists could find time to employ, must be regarded as an essential guide to the technical details necessary to complete work. Chapters on "Limnology," on "The Geographical Distribution of Organisms," on "Odors in Water Supplies," on "Storage of Water," on "The Growth of Organisms in Water Pipes," are followed by chapters on "The Classification and Description of Micro-organisms." A very useful bibliography and numerous unusually well-executed plates, wherein the experienced operator in this line of work will find many an old friend well portrayed and the beginner a very reliable guide, complete a work of much value to whom it may concern.

W. M. MEW.

THE SPIRIT OF ORGANIC CHEMISTRY. AN INTRODUCTION TO THE CURRENT LITERATURE OF THE SUBJECT. BY ARTHUR LACHMAN with an Introduction by PAUL C. FREER. The Macmillan Co. pp. xviii + 229. 12 mo. Price, \$1.50.

The point of view of the book is made evident by a few sentences from the Introduction: "How can he [the student] ever hope to master the general classification, let alone the minor details, which must become a part of his very being, if he too wishes to do his share, however small, toward completing and rounding out the still unfinished structure? The answer is plain: 'he can do this only by comprehending the *spirit of the science*, by learning its great theories, not as mere mnemonic efforts,

but as the result of a development for which many of the most earnest and acute minds known to the history of science have fought and toiled."

According to the preface the book is intended primarily as a supplement to text-books of organic chemistry. The author gives some with detail the views which have been held and now prevail on some of the leading questions in organic chemistry. These are the chapters: 1. The Constitution of Rosaniline; 2. Perkin's Reaction; 3. The Constitution of Benzene; 4. The Constitution of Acetoacetic Ether; 5. The Uric Acid Group; 6. The Constitution of the Sugars; 7. The Isomerism of Maleic and Fumaric Acids; 8. The Isomerism of the Oximes; 9. The Constitution of the Diazo Compounds.

E. H.

DIE CHEMISCHE ENERGIE DER LEBEN DEN ZELLEN. BY DR. OSCAR LOEW, U. S. Department of Agriculture, Washington, D. C. München, 1899.

This little volume of about 170 pages must be looked upon as a continuation of the investigations published by the author, treating of the difference between the living and dead forms of protoplasm.

The forerunners of the present publication are entitled respectfully, "Die chemische Ursache des Lebens," and "System der Giftwirkungen."

Though the titles would indicate entirely different subjects, they are yet the same in so far as Professor Loew has shown that poisons owe their power to their effect upon the living protoplasm, which is chemically a very active compound, but passes into a more stable product upon being deprived of life.

The book under discussion treats of the qualitative differences between living and dead protoplasm, and likewise the differences between various kinds of protoplasm. That these must exist is evident from many facts, as, for instance, that we possess some living organisms, which thrive at a temperature which is death to others. By physical differences as well as pathological and toxicological ones, the protoplasm of different organisms shows difference of behavior, which is exhibited by greater or less resistance to the action of chemicals. While the book contains mainly the author's own observations, it gives a place to those of others, with references to the literature, so that it can be looked

upon as a good exposition of the various views upon a subject, the development of which is due to the labors of the author himself. The observations are of so manifold a nature, that the perusal of the book cannot fail to be of value to all interested in the subject.

H. ENDEMANN.

A HISTORY OF PHYSICS IN ITS ELEMENTARY BRANCHES, INCLUDING THE EVOLUTION OF PHYSICAL LABORATORIES. BY FLORIAN CAJORI. New York and London: The Macmillan Co. 1899. viii+322 pp. 12mo. Illustrated.

In this convenient volume the author sketches the progress of the growth of mechanics, light, electricity and magnetism, meteorology and sound under the Greeks, the Romans, the Arabs, in Europe during the Middle Ages, and the Renaissance as well as through the succeeding centuries to the present time. There are also chapters on the atomic theory, the causes of failure of Greek physical inquiry, gunpowder and the mariner's compass, and the inductive method of scientific inquiry. The author feels that "some attention to the history of a science helps to make it attractive," and has written the book in hopes of stimulating students and teachers of physics. Dr. Cajori cites a sentence written by Ostwald, who points out as a "defect in the present scientific education of youth, the absence of the historical sense and the want of knowledge of the great researches upon which the edifice of science rests," and he hopes that this volume will assist in remedying the defect.

The necessity of limiting the book to 300 pages has caused great condensation of statement, and prevented elaboration of principles; students who wish, however, to pursue further special lines, will find abundant references to literature throughout the volume; these show a wide acquaintance with the sources of information on the part of the author. Biographical sketches of those who have distinguished themselves by their notable discoveries and inventions are among the features of the volume.

In looking through this record one cannot but notice the occurrence of national jealousy in respect to priority of discovery. Germany, France, England, Holland, Italy, and at a later period the United States of America, each puts in a claim for having taken the first step in several prime discoveries and

inventions. The cases of the thermometer and of the electric telegraph will occur to every one. In many cases the conflict for priority is due to the fact that similar thoughts occur independently to more than one person, and oftentimes an invention is a growth to which several individuals have contributed. Few philosophical instruments are perfect at their birth, the barometer being a notable exception.

Professor Cajori's book can be recommended to students who really want to master the historical aspects of physical science.

H. CARRINGTON BOLTON.

CHEMISTRY AND METALLURGY APPLIED TO DENTISTRY. BY VERNON J. HALL, PH.D., Professor of Chemistry and Director of the Chemical Laboratories in the Dental School and in the Woman's Medical School of Northwestern University. xii + 246 pp. Evanston, Ill.: The Technical Press. 1898.

There are, probably, many members of the American Chemical Society who will have but a vague idea as to the precise field which this book is designed to fill. For the benefit of such members, it may be said that the book is but one recognition of a general change in methods of instruction now actively progressing in dental schools; namely, the introduction of really meritorious courses in the sciences of pathology, anatomy, physiology, and chemistry, as necessary adjuncts to the purely practical courses in operative dentistry and dental prosthesis.

The metal work of dentistry being of such eminent practical importance to the profession, it naturally follows that metallurgy is that department of chemical teaching which is most emphasized in dental schools. Hence a demand for specialized textbooks on "dental metallurgy."

We do not think that the book before us is destined to take any prominent place in the development outlined above; unless, perhaps, as an adjunct to Professor Hall's lectures. Its laying out of a systematic laboratory course on the physical properties of metals is timely and meritorious; as is also the practice in the refining of certain metals. The work is decidedly weak, however, in two points: it is replete with partial truths, which are almost unavoidably uninformative or misleading; and it barely touches upon the philosophy of the subject-matter. It therefore fails as a compilation, or as an index to progress—both of which

results might be conserved in a book of equal size, provided ordinary quantitative physical and chemical data (which students cannot remember) were tabulated, and the space thus saved devoted to discussions of the rationale of essentials.

The quotation that follows has been selected at random, and fairly represents the general character of the statements. We find only this in explanation of cupels and cupellation: "cupels are small articles made of bone-ash and used in the process of cupellation. Bone-ash absorbs the oxides of almost all metals, particularly those of lead, hence it is used in purifying gold and silver, which do not oxidize."

G. H. MEEKER.

A TREATISE ON PHOTOGRAPHIC OPTICS. BY R. S. COLE, M.A., Late Scholar of Emmanuel College, Cambridge; Assistant Master, Marlborough College. Illustrated. New York: D. Van Nostrand Co. 1899. 330 pages. Price \$2.50.

This is a modern book covering in a very satisfactory manner the important principles of optics as applied in photography. The matter is divided into seven chapters treating of the General Theory of Light; Elementary Theory of Lenses; Aberration; Correction of Aberration and the Design of Lenses; Lens Testing; Exposures, Stops, and Shutters; Enlargement, Reduction, Depth of Focus, and Halation. As far as is possible, consistent with thoroughness, the discussion is carried on with the aid of very elementary mathematics only, the formulas and equations introduced corresponding to about what is found in our usual college courses in physics.

The chemistry of photography is not touched upon at all but in other directions the book contains much practical information, especially useful to the investigator or to the manufacturer of photographic apparatus rather than to the every-day commercial photographer. The scientifically inclined amateur who desires to get the best results from the appliances at his command or who wishes to improve understandingly on what he has, will find in this book much of the needed help. For example, the chapter on exposures, stops, and shutters explains, in a very concise way, the principles which should guide in the construction of shutters, and their action and efficiency in very short exposures and gives results which the student might otherwise have to search through many volumes of journals and annuals to find.

What is given on enlargement and reduction takes up practical details more fully than is true of other parts of the book and appears to be well-written and useful. On the whole the work can be heartily recommended to the class for which it is written.

J. H. LONG.

ANLEITUNG ZUR DARSTELLUNG CHEMISCHER PRAPARATE. Ein Leitfaden für den praktischen Unterricht in der anorganischen Chemie. VON PROFESSOR DR. H. ERDMANN in Halle. Zweite Auflage, mit 15 Abbildungen im Text. Frankfurt a. M.: H. Bechhold. 1899. viii + 92 pp.

The first edition of this book has won for itself a wide-spread reputation as a text-book for the preparation of chemical compounds. Dr. Erdmann is an exception to the general rule of German chemists. He is a firm believer in the supremacy of inorganic chemistry, and the methods he has introduced in the study of this subject will be acknowledged by most teachers as a progressive step. The author carefully points out in his preface to this edition that previous to the appearance of his book very little time was devoted in laboratory instruction in the preparation of inorganic compounds. Although it has always been recognized that the study of organic chemistry is best carried out by the preparation of a number of typical compounds, yet the experimental study of inorganic chemistry has mostly been limited to test-tube reactions. Dr. Erdmann has been a very active factor in changing this point of view, and the chemists of the inorganic schools both here and in Germany are requiring a more and more thorough drill in chemical preparations. Such a method brings out the manipulative skill and causes the student to exercise his experimental ingenuity more than any other thing in the study of chemistry. If students were required to make their chemicals on a scale sufficiently large for practical use, the majority of them would be better chemists. And it is not in the preparation of fanciful chemicals that the best education is obtained, but in the making and purification of the common substances which are met with every day. Another point which the author insists upon is the use of raw materials in sufficient quantity to give the student a good idea of the comparative amounts of final products obtained in each case; and this is a point which should not be overlooked, for production is a very essential factor in such a course. A

student who cannot obtain more than a one or two per cent. yield in the preparation of chemically pure sodium chloride, for example, will never make his living as a chemist. The synthesis of inorganic compounds is just as important a subject in that field as the synthesis of compounds in the organic field, but strange to say there are few very satisfactory text-books on this subject. We are overcrowded with volumes relating to the analytical side of inorganic chemistry, and but few teachers seem to have considered the other. But sometimes it requires more chemical knowledge and skill to build up a compound than it does to analyze it. The author has chosen his synthetic examples with good taste, and in most cases he gives methods which are of a practical nature. Another point of convenience and instruction which makes this volume something more than a mere recipe book is that the description of every preparation is accompanied by a clear explanation of the chemical reactions entering into the process, together with simple tests by means of which the purity of the compound obtained may be ascertained. There is one feature, however, which might be somewhat improved upon, and that is, references to the literature of the subject. In this edition, these are very limited, and consist for the most part of references to the author's own text-book on inorganic chemistry. Of course the majority of the methods described in this book, especially with regard to the details of precautions and the manner of manipulation, are original; but, nevertheless, there are other methods and other ideas on the same subject which should not be ignored, and a larger enumeration of references to the latest chemical literature would render the book more valuable and useful.

But on the whole, Dr. Erdmann has given us a book full of valuable matter, and his practical suggestions scattered so lavishly throughout the description of each preparation will be welcomed with delight by both teacher and student, and the volume deserves its title of "guide" in every sense of the word.

J. MERRITT MATTHEWS.

ERRATUM.

In the July (1889) issue, page 624, in lines 10, 7, and 4 from bottom, for "s = " read "S =".

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY
OF MICHIGAN, DR. A. B. PRESCOTT, DIRECTOR.]

THE DISTINCTION OF TRUE EXTRACT OF VANILLA FROM LIQUID PREPARATIONS OF VANILLIN.

BY WILLIAM H. HESS.

Received April 29, 1899.

AN "extract of vanilla" can not be made artificially that will duplicate the one made from the bean itself, either in respect to chemical behavior, or with regard to usefulness as a flavoring agent. During the sweating process in preparing the vanilla bean for market, chemical changes of unknown nature take place, and as a result of these changes, the aroma is much improved. The importance of this process is well known, and those conditions which produce the best flavor are carefully studied.¹ To provide the various ingredients of the vanilla bean artificially and so treat them that the delicate aroma incorporated in an alcoholic tincture shall equal that acquired from the bean is a hopeless task, and it is quite as difficult to deceive the analyst by such a product. The vanillin that is synthesized and put upon the market, is identical with the vanillin extracted from the bean itself. There are other constituents as tannin, gum, and organic acids which might be duplicated, and whose origin could not be easily proved. There is one important constituent, however, which will be extremely difficult to replace, and that is the

¹ See article by Prof. H. H. Rusby, Merck's Report, Feb. 1, 1898, p. 74.

resin. This resin behaves so differently from other resins that its separation and identification is a most valuable means of proving the origin of "vanilla extract."

Vanilla beans contain from four to eleven per cent. of this resin. It is of a dark red to brown color. The coloring-matter furnished by this resin constitutes about one-half of the color of the tincture of vanilla. Since manufacturers desire a deeply colored product, they are careful to get all the resin in solution. This resin is soluble in fifty per cent. alcohol so that in the "extract" of high grade where plenty of alcohol is used, all the resin is kept in solution. In cheap extracts where as little as twenty per cent. of alcohol by volume is sometimes used, an alkali, usually potassium bicarbonate, is added to aid in getting resin, gum, etc., in solution, and also for the purpose of preventing subsequent turbidity. The color is thus deepened very materially. As vanillin is acidic in character and decomposes carbonates to form salts, the delicate flavor is impaired to a considerable extent by the addition of an alkaline carbonate, and a foreign odor is thereby introduced that is quite disagreeable and not difficult to recognize.

In testing preparations of vanilla it is well to make a pharmacopoeial tincture to be used in parallel tests, along with the sample of unknown purity. The following simple tests have been found useful:

I. DILUTION TEST.

Place a few cc. of the alcoholic tincture in a test-tube and add water slowly to three times the original volume and shake. If no alkali has been used in making the extract, a flocculent reddish brown precipitate will separate out. There should be but a slight turbidity. A milky solution would indicate foreign resin. Now add hydrochloric acid, a drop at a time, to a portion of the diluted sample. Turbidity results at once, due to extracted matter held in solution by the plant bases, as well as by alkali purposely added. The turbidity produced on acidifying should be slight (absence of foreign resin). Some practice with this simple test will enable an inspector to judge somewhat of the character of a "vanilla extract." If alkali have been used,

the turbidity increases considerably, and the *color* will fade when acid is added.

2. SEPARATION AND IDENTIFICATION OF THE RESIN.

Place 25 cc. of the "extract" to be examined in an evaporating dish and drive off the alcohol on a water-bath. When the alcohol is all gone, make up to about the original volume with water. If alkali have not been used in the manufacture of the "extract," the resin will appear as an amorphous, flocculent, red to brown residue. Acidify the cool solution with a few drops of hydrochloric acid to free the resin from bases, and the whole of the resin will separate out leaving a partly decolorized and clear supernatant liquid, after standing a short time. If it is desirable to weigh the resin for a quantitative determination, several hours are necessary for its complete separation. Collect the resin on a filter, wash with water, and reserve the filtrate for further tests.

Place a piece of the filter with the resin attached in a few cc. of dilute caustic potash. The resin dissolves to a deep red solution. On acidifying, the resin is reprecipitated.

Make a solution of the resin in alcohol. To one portion of this alcoholic tincture add a few drops of ferric chloride. No striking coloration is produced. To another portion of the alcoholic tincture add some hydrochloric acid, and again there is little change in color. Most resins give color reaction with ferric chloride or hydrochloric acid in alcoholic solution.

3. TESTS OF COLORING-MATTER.

(a) *For caramel*.—Concentrate a portion of the filtrate obtained from the resin in an evaporating dish on a water-bath until the depth of color is approximately that of the original tincture. Now add a few drops more of strong hydrochloric acid (nitric or dilute sulphuric acid will also serve), and heat gently. If caramel be present a yellowish red, flocculent precipitate is formed, very much resembling a precipitate of iron hydroxide in color and texture. Cool and filter out this precipitate, and wash it with water. It is insoluble in water, strong alcohol, or ether. It is soluble in dilute caustic potash, in gla-

cial acetic acid, and in dilute alcohol. About one half the color of caramel is thus removed.¹

(b) *For an azo dye.*—To a small portion of the filtrate add some ammonia. With a natural product the color is very much deepened. Now add some zinc dust and let it digest. The color should not fade entirely even on heating, but the solution will assume a tint about as deep as it was before adding ammonia. If the coloring be due to an azo dye it will fade to a colorless solution, the azo being reduced to the hydrazo compound. Pour some of the decolorized product into an open dish so as to expose considerable surface of liquid to the oxygen of the air. In case an hydrazo group has been formed, it will be slowly oxidized back to the colored azo compound. The oxidation may be hastened by adding some hydrogen peroxide, and the color will return at once. Other reducing agents as stannous chloride and hydrochloric acid, will also serve.

Test a portion of the original solution from the resin for tannin. This substance is present in small quantity only, and should not be found in great excess.

To another portion of the sample add a few drops of lead acetate solution. A bulky flocculent precipitate should form, showing the presence of organic acids and extractives in considerable quantity. This test should be the first, and absence of a precipitate condemns the sample. This precipitate will carry with it nearly all the coloring-matter left in the filtrate from the resin.

Vanilla extract is frequently adulterated with the "Extract of Tonka." The sophistication is best detected by ascertaining the presence of coumarin, the odoriferous constituent of the tonka bean. For a quick method of detecting coumarin in presence of vanillin, see a previous paper from this laboratory.²

¹ For further tests for caramel see Author in *Ztschr. anal. Chem.* (1885), p. 30. The following method for caramel and resin will be found most convenient and satisfactory in examining commercial extracts. If the solution, free from alcohol, is acidified slightly with hydrochloric acid and digested a few minutes on a water-bath, both the resin and caramel will be precipitated. Now filter, wash well with water to remove all sugar, and dry the precipitate and filter-paper at a low temperature. Treat the precipitate with absolute alcohol as long as any color is washed out. This removes the resin and leaves the caramel on the filter. The alcohol may be evaporated from the resin and the latter may then be treated as above. The residue is easily proved to be caramel by dissolving it in hot dilute acetic acid and adding phenylhydrazine to the solution, when a reddish brown precipitate will form which is characteristic at this point.

² This Journal, 21, 256 (1899); *Pharm. Review*, 17 (Jan., 1899).

This investigation has been made at the request of Prof. Albert B. Prescott, to whom I wish to express my thanks for counsel in the work.

UNIVERSITY OF MICHIGAN, April 25, 1899.

[CONTRIBUTIONS FROM THE LABORATORY OF LAFAYETTE COLLEGE.]

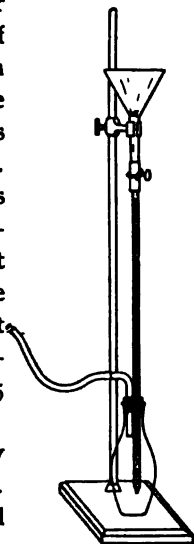
A SIMPLIFIED REDUCTOR.

BY P. W. SHIMER.

Received June 3, 1899.

FOR the reduction of iron and phosphomolybdate solutions, I have been using, for some time, a form of reductor which is simple, convenient, and effective. The reductor tube is a plain glass tube three-eighths inch in internal diameter and twenty inches long, drawn-out and cut off at the lower end. It is filled by placing a few small pieces of broken glass in the drawn-out portion and on this about an inch of well-cleaned sand. The tube is then filled with amalgamated zinc of as nearly uniform twenty mesh size as possible. About eighty grams are required. No asbestos or glass wool is used. The sand prevents particles of zinc from falling through, and it does not become clogged by use. Should any error arise on account of the omission of a more perfect filter, it would show in the blank, which is, however, uniformly very small, not more than 0.05 to 0.10 cc. permanganate.

The use of amalgamated zinc, as proposed by A. G. McKenna, makes a small reductor possible. The consumption of zinc is very small, and when the column has settled about one inch, a little fresh zinc can easily be poured in above. The reductor tube is united with a four-inch funnel by means of rubber tubing, well tightened with wire. Between the funnel and reductor is a Hoffman clamp. The lower end of the tube passes through a soft two-hole stopper so far as to reach half way to the bottom of a heavy-walled pint gas-bottle. The gas-bottle is connected with a filter-pump through an intermediate safety-bottle and valve. The funnel is clamped to a retort stand in such a



manner as to allow the tube and gas-bottle to swing easily in all directions. It is well to so adjust the height as to leave the gas-bottle raised slightly above the base. The passage of the solution through the reductor may be effected either by use of the pump, or by means of the vacuum obtained by condensation of steam, devised originally in Bunsen's laboratory. In using the latter method a little water may be boiled in the gas-bottle until all air is expelled and then quickly unite with the reductor, the clamp on the filter-pump tube being closed. The speed of filtration is regulated by the upper clamp. Instead of filling the gas-bottle with steam by boiling water in it, it is better to have a convenient tin or copper can containing boiling water and provided with one or more short steam outlet tubes on top. The empty gas-bottle is inverted over one of these steam outlets and, when filled with live steam, is taken off and united as quickly as possible with the reductor. This latter method has the advantage of starting with an empty gas-bottle, which is desirable, on the score of accuracy, both in iron and phosphorus determinations. When a large number of reductions have to be made, a number of reductors may be used, and, with a steam vessel provided with a number of outlets, gas-bottles may always be ready for reductions.

The hot lower part of the reductor in the gas-bottle is particularly effective in perfecting the reduction of phosphomolybdate solutions. The reduction is to Mo_3O_8 , and the factor is 0.88163.

A few phosphorus determinations are the following :

No.	Volumetric.	Gravimetric.
1	0.041	0.041
2	0.0155	0.017
3	0.098	0.098
4	0.040	0.039

A few iron determinations in Alabama red ore are as follows : 48.52, 48.52, 48.51, 48.46, 48.52.

By reduction with five grams zinc in a flask the result on this ore was 48.45.

The speed of filtration through the reductor should not be too rapid. From three and a half to five minutes should be allowed for a reduction.

ON VAN'T HOFF'S EQUATION AND THE MOLECULAR WEIGHTS OF LIQUIDS.

By C. L. SPEYERS.

Received May 9, 1899.

CONSIDER the equation

$$\frac{n}{N+n} = \frac{p-p'}{p} \text{ or } \frac{n}{N} = \frac{p-p'}{p'}, \quad (1)$$

where n is the number of gram-molecules of solute, N is the number of gram-molecules of solvent calculated from the ordinary molecular weight, that is, the molecular weight of the solvent in the solution, *not* the molecular weight of the solvent in the vapor state between pressures p and p' , and p and p' are the vapor-pressures of pure solvent and solution, respectively.

Consider also the equation

$$\frac{n}{N} = \frac{p}{p'}, \quad (2)$$

where N is now calculated from molecular weight of the solvent in the vapor state between pressures p and p' , the other letters being the same as for equation (1).

When p' is only a trifle smaller than p , then the two equations are just about equivalent, but they are not at all equivalent when p' is quite different from p . In the applications of these equations the difference $p - p'$ has hitherto been small and either equation has answered for the purposes desired. But recently the vapor-pressures of some concentrated solutions have been measured and for these solutions, equation (2) seems to fail lamentably while equation (1) seems to give excellent results.

The vapor-pressures have been measured by Noyes and Abbott,¹ by Goodwin and Burgess,² by Linebarger,³ and by Lehfelddt.⁴

Noyes and Abbott, and Goodwin and Burgess, used solutions of naphthalene, azobenzene, benzophenone, and diphenylamin, in ether. The concentrations of their solutions ran up to about fourteen per cent. gram-molecules of solute.

When curves are plotted from equations (1) and (2) for which

¹ *Ztschr. phys. Chem.*, 23, 56 (1897).

² *Ibid.*, 28, 99 (1899).

³ *This Journal*, 17, 615, 690 (1895).

⁴ *Phil. Mag.*, 46, 42 (1898).

curves p' is the ordinate and the per cent. gram-molecules is the abscissa, the values obtained from each curve agree pretty well with experiment, so long as the solutions are dilute, but as the solutions grow more concentrated, the deviation from observation increases, and the deviation increases more markedly with p' calculated from (2) than with that calculated from (1). In making such comparison we must of course assign a molecular weight to the solute. I assigned a normal molecular weight to each solute. Had a different molecular weight been assigned to the solute, and I think for naphthalene at any rate we certainly ought to have done so, then the calculated values for p' could be made to agree with the observed values. So these experiments do not declare strongly against either equation. But the observations of Linebarger and of Lehfelddt will compel us to reject (2) in favor of (1). They used liquids miscible in all proportions so that we can follow the molecular weights of solvent and solute from infinite dilution to complete purity. How equation (1) is to be applied, I have tried to show.¹

Mixtures of chlorbenzene with benzene, chlorbenzene with toluene, brombenzene with benzene, carbon tetrachloride with toluene, when plotted with vapor-pressures as ordinates and per cent. gram-molecules as abscissas, all have partial vapor-pressures so nearly straight lines that we seem compelled to go further and put them as straight lines. This means that the molecular weight of the solute does not change at all with concentration; therefore, we must assume that the molecular weight of the solute in such solutions is normal, for whenever we can follow a molecular weight that is not normal, we find that it is variable with the concentration.

If we claim that equation (1) is not applicable but that equation (2) is the correct one to use, and that the molecular weight of the solute varies in such way that (2) is possible, then we are led to absurd values for the molecular weight of the solute.

Let w be the weight of the solute, W be the weight of the solvent, m be the molecular weight of the solute, M be the molecular weight of the solvent; then,

$$n = \frac{w}{m} \text{ and } N = \frac{W}{M},$$

¹ *J. phys. Chem.*, 2, 347 (1898); *This Journal*, 21, 282 (1899).

and we have from (1)

$$m = \frac{Mw}{W} \frac{p'}{p - p'} \quad (3)$$

and from (2),

$$m = \frac{Mw}{W(lp - lp')} \quad (4)$$

Let us apply these equations to the mixture of benzene and acetic acid at 35°, using data recalculated¹ from Linebarger's experiments. The following table contains these data :

HC ₂ H ₃ O per cent. gram-mole- cules.	C ₆ H ₆ per cent. gram- molecules.	V. P. HC ₂ H ₃ O ₂ (26.5).	V. P. C ₆ H ₆ (146).	Mol. wt. C ₆ H ₆ by (3).	Mol. wt. C ₆ H ₆ by (4).	Mol. wt. HC ₂ H ₃ O ₂ by (3).	Mol. wt. HC ₂ H ₃ O ₂ by (4).
10	90	2.8	140	78	312	156	158
30	70	8.0	127	78	152	172	184
50	50	13.2	109	78	112	177	205
70	30	18.7	85.8	78	87.7	199	263
90	10	23.8	45.0	78	84.1	241	459
93	7	24.6	34.3	78	78.9	245	550
96	4	25.2	22.5	78	63	262	770
98	2	25.9	12.6	78	68.7	278	1200

The molecular weight of benzene is not absurd as calculated by either formula, though suspiciously low by formula (4) in solutions dilute with respect to benzene. The molecular weight of acetic acid keeps within acceptable range as calculated by formula (3), while it runs far beyond acceptable range as calculated by formula (4).

Equation (4) as originally obtained by van't Hoff² was limited to solutions so dilute that the heat involved in removing the necessary quantity of solvent was negligible. This heat of course is not the heat equivalent of the osmotic work, but the heat of dilution at constant concentration minus the heat equivalent of the osmotic work.

Let us now deduce equation (4) again, following van't Hoff in a general way but using solutions as concentrated as we choose, only requiring that the quantity of solution shall be so great that no appreciable change in concentration may be made when the necessary quantity of solvent is removed or added. That component whose vapor-pressure is measured shall be considered as the solvent.

¹ *Loc. cit.*

² *Ztschr. phys. Chem.*, 1, 481 (1887).

We carry out an isothermal reversible cycle with the usual arrangement of a cylinder with frictionless piston, one end of the cylinder being closed by a diaphragm permeable to the solvent but not to the solute. Inside the cylinder is the large quantity of solution, outside the cylinder is the pure solvent. Temperature is equal to T . We press down on the piston. Thereby the solution is compressed until the pressure on it reaches the osmotic pressure π . Let β , be the coefficient of compression of the solution defined by

$$\beta = \frac{dv}{dp} \cdot \frac{1}{v}.$$

The work of this compression is

$$+ \int_{p_1}^{\pi} V\beta, d\pi,$$

where V is the initial volume of the solution and p_1 is the vapor-pressure of the solvent over the solution.

We continue pressing, and the pure solvent now passes out. The work is kept up until so much of the solvent has passed out as contained one gram-molecule of solute; that is, N/n gram-molecules of solvent are pressed out. The work of this operation is

$$+ \pi \varphi$$

where φ is the volume of the N/n gram-molecules of solvent.

After the solvent has passed through the diaphragm, it is released from the osmotic pressure and consequently expands, returning the work

$$- \int_{p_1}^{\pi} \varphi \beta, d\pi, \quad (5)$$

where β_1 is the coefficient of compression of the pure solvent, and p_1 is the vapor-pressure over the pure solvent. It seems to me from what I have previously said¹ that we should in each case consider the coefficient of compression of the pure solvent only as entering into the operations, and not that of the solution at all. However, even if we do make a distinction in the two coefficients, the difference thereby introduced is vanishingly small, and we need not discuss this matter in any detail.

¹ This Journal, 22, 579 (1898).

Heat energy, aside from the heat equivalent of the osmotic work, may be involved when the solution and solvent are separated, as already pointed out. Let Q be the heat involved when one gram-molecule of solvent is added to the solution under consideration. Then the heat involved in separating solution and solvent in the above operation is

$$\pm \frac{N}{n} Q.$$

The N/n gram-molecules of solvent are now vaporized isothermally at T . The work of this is

$$-p_1 v_1,$$

where v_1 is the volume of the vapor under p_1 pressure.

The vapor is now expanded isothermally to the volume v , corresponding to p , pressure. The work of this is

$$- \frac{N}{n} R T \ln \frac{p_1}{p},$$

where R is of course the gas constant.

The vapor is now brought into contact with the solution. But before this can be done, the pressure previously on the solution must be removed. In so doing the system returns nearly all the compression work, the slight deficiency in the return being due to the loss of the N/n gram-molecules of solvent, a deficiency which is very small even when at its maximum value but which in the present case is still smaller since a large part of the compression work belonging to the removed solvent has already been returned by the system, (5). The compression work now returned by the system is

$$- \int_{p_1}^p (V - \varphi) \beta_1 d\pi.$$

The solution is now ready to receive the vapor. The work of driving it in is

$$+ p_1 v_1.$$

Now if heat is involved in separating solvent and solute osmotically in the first operation, then the same quantity of heat

but with opposite sign must be involved when the vapor is driven into the solution. So we have

$$\mp \frac{N}{n} Q.$$

Of course, this heat has nothing to do with the heat of condensation.

The isothermal reversible cycle is now complete and so,

$$\begin{aligned} + \int_{p_1}^{\pi} V \beta_1 d\pi + \pi \varphi - \int_{p_1}^{\pi} \varphi \beta_1 d\pi \pm \frac{N}{n} Q - p_1 v_1 - \frac{N}{n} R T l \frac{p_1}{p_s} \\ - \int_{p_1}^{\pi} (V - \varphi) \beta_1 d\pi + p_1 v_1 \mp \frac{N}{n} Q = 0, \end{aligned}$$

and since for our purpose,

$$\int_{p_1}^{\pi} V \beta_1 d\pi = \int_{p_1}^{\pi} \varphi \beta_1 d\pi + \int_{p_1}^{\pi} (V - \varphi) \beta_1 d\pi,$$

we have

$$\pi \varphi = \frac{N}{n} R T l \frac{p_1}{p_s}$$

or

$$\frac{n}{N} = l \frac{p_1}{p_s}$$

as before.

It would appear then that the compressibility of the solution need not be considered, neither need the heat of solution be considered so far as this is independent of the osmotic work, a conclusion which is not in accord with that of others. Yet I cannot see what is wrong in my deduction, and I reach the same result when I follow Gouy and Chaperon,¹ for I cannot see how the vapor can be returned to the solution without releasing the pressure on it, nor how the solvent can be vaporized without releasing the pressure on it. Likewise the heat of separation seems to cancel with heat of mixing when the vapor is driven into the solution in the last operation.

In Arrhenius' method² of getting the osmotic pressure, the com-

¹ As given in Winkelmann's "Handb. d. Physik.," I, 633.

² *Ztschr. phys. Chem.*, 3, 115 (1889).

pressibility of the solution likewise seems to disappear. The column of solution rises to a certain height h . The osmotic pressure is

$$\pi = hs,$$

where s is the density of the solvent.¹ When the column is so high that the hydrostatic pressure is considerable, the lower layers of liquid become more dense and hence a greater mass of liquid in the vertical column and apparently a greater osmotic pressure. But the pure solvent as it passes through the diaphragm is compressed itself and so its concentration is increased which balances the increased concentration of the solvent in the solution, using the word concentration in the sense of mass in unit volume. Similarly the concentration of the solvent in any particular layer of the solution is greater than the concentration of the solvent in any layer above that particular layer, and therefore will exert a pressure from the lower layer upwards, which upward pressure is proportional to the difference in concentration of the two layers and therefore to the density. The solute itself is of course equally distributed throughout the column of liquid. So it would seem to me that, although the mass in the column of solution is increased by the compression, yet the solvent as it enters becomes compressed, its concentration is increased, and therefore its osmotic activity is likewise increased, and we have as the measure of osmotic activity, only the concentration of the solute whatever the compression may be.

I do not see therefore where we can find any substantial correction for equation (2) so as to bring it into accord with observation. A correction may be brought in by considering that N refers to the molecular weight of solvent in the vapor state. In that state, the molecular weight is frequently somewhat greater than the simple chemical formula would give. Referring to formula (4) as applied to acetic acid as solute in benzene as solvent we see that an increase in M only makes matters worse, but that as applied to benzene as solute in acetic acid as solvent an increase in M would improve matters for solutions dilute in respect to benzene. Another correction may be brought in by considering that $RT \ln \frac{p}{p'}$ is only a true expression of work when

¹ This Journal, 22, 579 (1898).

the gases are true gases, and the vapors we are considering are by no means true gases. However, for all vapors which I could follow in tables, the corrections coming from this source were trifling.

I do not mean of course that equation (2) is wrong; I only mean that it does not give results in harmony with our ideas concerning the molecular weights of liquids in concentrated solutions, while equation (1) does give excellent results, and I cannot find sufficient reason why (2) should fail unless we look upon the osmotic laws as ideal laws to be kept out of actual experimental work.

We cannot at present therefore base equation (1) on equation (2), but must seek some other way of justifying it, a conclusion not reached in a previous paper.¹

RUTGERS COLLEGE,
May 6, 1899.

HYDRASTINE HEXAIODIDE, AND THE ASSAY OF HYDRASTIS CANADENSIS BY MEANS OF STANDARD IODINE FOR HYDRASTINE AND OF STANDARD POTASSIUM IODIDE FOR BERBERINE.

BY H. M. GORDIN AND A. B. PRESCOTT.²

Received May 11, 1899.

WHEN a solution of iodine in potassium iodide is added to a solution of a salt of hydrastine a dense precipitate falls out, of a color varying from light brown to a very dark brown. In this order of mixing the alkaloidal solution with the iodine solution, different periodides seem to be formed in mixture, no matter whether the addition of iodine is stopped while the alkaloid is yet in excess or carried till the iodine is in excess. Even in the first case, that is, when the addition of iodine is stopped long before all the alkaloid is precipitated, the body formed only approaches a triiodide in composition, but does not correspond to a triiodide exactly. As will be seen from the accompanying analysis the total iodine of the periodide formed under these circumstances agrees quite well with the theoretical amount required by hydrastine triiodide, but the additive iodine is considerably below the amount required by that body. It

¹ *J. phys. Chem.*, 2, 358 (1898).

² In the work of Research Committee D, Section II., Revision and Publication of the Pharmacopoeia of the United States.

will be noticed that there is a decided difference in this respect between hydrastine on one hand, and strychnine, brucine, and some other alkaloids on the other. The latter always form triiodides when iodine is added to an excess of a solution of their salt.¹

But if the order of mixing be reversed, that is, the weak alkaloidal solution added to a large excess of iodine, a definite and unique periodide, namely, hydrastine hydriodide pentaoidide is always formed. This body is prepared according to the general method of making the higher alkaloidal periodides, described by us in the previous paper.² The hexaiodide thus made is a very dark brown powder, very difficultly soluble in ether, benzol, or cold chloroform, more readily in hot chloroform and in alcohol, and very easily in a mixture of alcohol and chloroform, or of alcohol and ether. In hot water it melts to a resinous mass. Attempts to crystallize it have failed, as on evaporation of the solvent it always remains a resinous mass.

Both in the hydrastine hexaiodide and the lower compound, that approaching a triiodide in composition, the so-called additive iodine was estimated by dissolving the substance in a small quantity of a mixture of alcohol and chloroform, and titrating with standard sodium thiosulphate. For the estimation of total iodine in these compounds, the substance was treated with zinc and ammonia, the iodine then liberated by means of a solution of nitrous acid in concentrated sulphuric acid, and taken up with carbon disulphide. The details were carried out exactly as described in our paper on morphine tetraiodide.³

ANALYSIS OF THE HYDRASTINE HEXAIODIDE.

For additive iodine: 0.1371 gram substance was found to contain 0.075833 gram additive iodine, and 0.1623 gram substance, 0.0898344 gram additive iodine.

Calculated for $C_{11}H_{11}NO_5HI_6$.	I.	Found.	II.
55.43	55.30		55.34

For total iodine : 0.1491 gram substance contained 0.0996800 gram total iodine, and 0.1429 gram contained 0.0958333 gram total iodine.

¹ This Journal, 20, 708 (1898).

² *Loc. cit.*, 710 (1898).

³ This Journal, 20, 717 (1898).

Calculated for $C_{21}H_{21}NO_6HI.I_2$.	I.	Found.	II.
66.52	66.86		66.06

ANALYSIS OF THE LOWER PERIODIDE OF HYDRASTINE,
APPROACHING A TRIIODIDE.

For total iodine: 0.2674 gram contained 0.1337328 gram total iodine, and 0.2396 gram contained 0.1191752 gram total iodine.

Calculated for $C_{21}H_{21}NO_6HI.I_2$.	I.	Found.	II.
49.83	50.01		49.74

For additive iodine : 0.09535 gram contained 0.0340975 gram free iodine, 0.1737 gram contained 0.0626681 gram free iodine, 0.1215 gram contained 0.04413953 gram, and 0.2328 gram contained 0.0838545 gram free iodine.

Calculated for $C_{21}H_{21}NO_6HI.I_2$.	I.	II.	Found.	III.	IV.
33.22	35.76	36.07		36.33	36.02

In the iodometric estimation of hydrastine the exclusive formation of the hexaiodide is assured by adding a weak solution of the alkaloidal salt to a large excess of iodine. The estimation is carried out in the same way as described by us in a previous paper.¹

The factor for hydrastine is 0.60403.

$$382.14 : 5 \times 126.53 :: 0.60403 : 1$$

In order to test this factor two solutions of hydrastine² in acidulated water were prepared, containing 0.3 per cent. and 0.15 per cent. of the free alkaloid, respectively, and the estimation of the strength of the solutions carried out exactly as described in the above-mentioned paper.

The results were as follows: Twenty cc. of the first (three-tenths per cent.) solution consumed 0.0970001 gram free iodine and twenty-five cc. of the second (0.15 per cent.) solution consumed 0.0611461 gram free iodine.

STRENGTH OF THE SOLUTIONS.

	Actually contained.	Found.
1	0.30	0.29
2	0.15	0.14

¹ This Journal, 20, 722 (1898).

² We are indebted to Prof. John Uri Lloyd, of Cincinnati, for a specially prepared sample of hydrastine. We had also a sample furnished us in a lot of pure alkaloids by Merck & Co. These two samples agreed very well with each other in the quantitative results.

PLAN OF THE ASSAY OF HYDRASTIS CANADENSIS.

The estimation of hydrastine and berberine in this root is based upon the following principles :

1. Hydrastine is quite soluble in absolute ether and forms, as we have just shown, a definite hexaiodide when a weak solution of any of its salts is added to a large excess of iodine dissolved in a potassium iodide solution.

2. Berberine on the contrary is completely insoluble in *absolute* ether.

This can be shown by rubbing up some pure berberine in a mortar with absolute ether, filtering, evaporating the ether and taking up with acidulated water. The liquid thus obtained is perfectly colorless and no trace of turbidity is produced in it, by Mayer's reagent, Wagner's reagent, or picric acid, nor does chlorine water produce the characteristic rose band.

3. Of all the difficultly soluble berberine salts the hydriodide seems to be the least soluble, particularly so in a very large excess of potassium iodide. If to a solution of berberine in water slightly acidulated with acetic or sulphuric acid, a large excess of a potassium iodide solution be added, the precipitation is so complete that the filtrate is almost entirely colorless, and no alkaloid can be detected in it by any of the above-mentioned reagents. Even chlorine water, reacting with a delicacy said to be one in 250,000, does not give any coloration, after removal of potassium iodide from the filtrate by silver nitrate, and of the excess of the latter by hydrochloric acid.

4. If to a very dilute solution of a salt of pure berberine about ten to fifteen times its amount of acetone be added and the solution then made strongly alkaline with solution of sodium hydroxide, berberine-acetone is so fully precipitated, particularly after ten or fifteen minutes' shaking, that the filtrate is almost completely colorless and no traces of alkaloid can be detected in it, after acidulation, by means of the above-mentioned reagents.¹ This berberine-acetone is easily decomposed by boiling with mineral acids, with the liberation of pure berberine.

These statements about berberine are true only when the berberine is perfectly pure, such as can be obtained from berberine-

¹ The compound of berberine with acetone was first made by Gaze: *Arch. d. Pharm.*, (1890), 607.

acetone according to the directions of Gaze¹ and dried in the air without heat. Commercial salts of berberine and particularly commercial berberine itself is generally so impure that some of these reactions will not hold good.²

Basing ourselves upon these facts we have worked out a

¹ *Loc. cit.*

² Beside berberine and hydrastine one other alkaloid has been found in Hydrastis, but in proportions quite too small to have any bearing upon the assay percentages, either of berberine or hydrastine. That the assay process here proposed leaves no appreciable quantity of any alkaloid behind we have verified by operating upon a considerable quantity of the drug. After removing the hydrastine with the ether and the berberine with potassium iodide, there was nothing left that gave indications of alkaloidal character. What has been learned of canadine makes it probable that it would adhere to berberine or to hydrastine. In the elaborate research which has established the existence of canadine, Prof. E. Schmidt (*Arch. d. Pharm.*, 232, 136 (1894)) prepared it from a crude hydrastine, and also from a crude canadine hydrochloride made for him by E. Merck, of Darmstadt. In the purification the canadine was precipitated as a salt of nitric acid. The insolubility of its salts with mineral acids would be likely to carry it into the crude salts of berberine, when these are precipitated for the removal of this alkaloid. Prof. J. U. Lloyd ("Drugs and Medicines of North America," Cincinnati, pp. 139-141, 127 (1885)), has shown that strong acidulation with hydrochloric acid is necessary to the full precipitation of the berberine, and that when the filtrate is precipitated by ammonia at the neutral point, any further precipitation caused by an excess of ammonia consists of or contains berberine, as a result of its incomplete removal by acid precipitation. Prof. Lloyd was evidently right in his conclusion that the method of Burt (*Am. J. Pharm.*, 47, 481 (1875), for "a third alkaloid" yields berberine unless this has been more closely removed by the strong acidulation just referred to. But since the research of Schmidt it appears likely that canadine would be precipitated with the berberine by strong acidulation. And the discrepant accounts of the color of the third alkaloid are explained by the discovery that though it is colorless, in purity, it acquires color by exposure to light and air, tetrahydroberberine ($C_{20}H_{21}NO_4$) being oxidized into berberine itself ($C_{20}H_{19}NO_4$) (Schmidt: *Arch. d. Pharm.*, 232, 148 (1894)). However, neither Hale nor Burt worked with enough of the Hydrastis to obtain canadine in the purity and amount required for any satisfactory description or conclusion. They did not claim to individualize or name the alkaloid; indeed the note of Hale only raised the question of its existence. Prof. Schmidt, who had, as he said, worked more than ten years with Hydrastis alkaloids, found it needful to operate upon fifty kilograms of the drug, and availed himself of a crude product accumulated in a manufactory. This was about five years after Wilhelm had made a report from the laboratory of Prof. Schmidt (*Arch. d. Pharm.*, 226, 330 (1888)), upon a third alkaloid in Hydrastis. In this report the finding of this alkaloid was ascribed to Hale (*Am. J. Pharm.*, 45, 247 (1873)), Burt (*loc. cit.*), and Lerchen (*Am. J. Pharm.*, 50, 470 (1878)), and the reader might infer that the name, canadine, had been proposed by Hale and Burt. Consequently in the second edition of "Beilstein" (III, 491) "canadine" is described upon no other authority than that of Hale and of Burt. In Beilstein's third edition, with fuller description, the authority of E. Schmidt, Privatmitth., is prefixed. The alkaloid examined by Wilhelm in 1888, not analyzed because of insufficient quantity, was prepared from ammoniacal solution by extraction with acetic ether. That observed by Hale, by Burt, and by Lerchen was obtained by precipitation with ammonia in some excess. The first elementary analysis was made by L. Deichmann (Inaugural dissertation, Rostock, 1892). In the analysis of Schmidt his figures differ from those of Deichmann, from greater purity of preparation (*Arch. d. Pharm.*, 232, 139 (1894)). Deichmann reported a cryoscopic determination of the molecular weight. Zeisel (Inaugural dissertation, Dorpat, 1892) determined the methoxy groups in canadine.—A. B. PRESCOTT.

method of assaying *Hydrastis Canadensis*, the plan being as follows: The alkaloids of the powdered root are first set free by the action of an ether-ammonia mixture, consisting of stronger ammonia water five cc., alcohol five cc., and ether thirty cc.¹ After drying, the powder is extracted with absolute ether and the ethereal extract, after evaporation of the ether and taking up the residue with acidulated water, is used for the estimation of hydrastine by any suitable method. Through the powdered root left in the extraction apparatus air is passed till it is dry, and then the powder is extracted with alcohol to exhaustion. The alcoholic extract, after dilution with water, evaporation of the alcohol and taking up the residue with diluted acetic acid, is used for the estimation of berberine. The berberine is first precipitated as berberine-acetone, the latter washed, decomposed by the aid of acid, and the purified berberine estimated by standard solutions of potassium iodide, silver nitrate, and ammonium thiocyanate.

DIRECTIONS FOR THE ASSAY.

Ten grams of the finely powdered *Hydrastis* are rubbed up to a paste with a few cc. of the above-mentioned ether-ammonia mixture in an eight ounce, screw-top ointment jar, and a few cc. more of the same mixture are then added so as to have the powder well covered with liquid. The small pestle is then left inside, and the jar well covered is set aside over night. The jar is then opened, put into a good current of air till the odor of ammonia has disappeared, and then in a vacuum over sulphuric acid for about five or six hours. The powder is then put into a filter-paper cell, placed in a Soxhlet extraction apparatus, the jar rinsed out several times with powdered glass or in the absence of this with coarsely powdered barium nitrate, the rinsings added to the Soxhlet, the latter connected with an Erlenmeyer flask containing about forty or fifty cc. absolute ether, and the extraction conducted in the usual way, till a few drops after evaporation of the ether and acidulation give no reaction with Mayer's or Wagner's reagent. The ethereal extract will be found to

¹ This is the same mixture we have used in our general method of extracting alkaloids (This Journal, 21, 232 (1899)), with the omission of chloroform. The latter gives with berberine a compound not decomposable by acids (E. Schmidt. *Pharm. Ztg.*, (1887), 542).

have only a very slight yellow color. The Erlenmeyer is then detached from the Soxhlet, the ether poured out into a flat evaporating dish, the Erlenmeyer washed out several times with water containing about two per cent. sulphuric acid, the washings added to the contents of the evaporating dish, and the latter put into a draught at about 30° C. till the ether has disappeared.

The contents of the dish are poured into a 100 cc. flask, the dish washed, the washings added into the flask and the latter filled up to the 100 cc. mark. The solution containing hydrastine sulphate, and of which every ten cc. represent one gram of the root, is used for the estimation of hydrastine.

For the iodometric estimation twenty cc. of the filtered solution (representing two grams of the drug) are run from a burette into a 100 cc. flask containing twenty or thirty cc. of a standardized solution of iodine of any known strength (that in the neighborhood of one per cent. is the best) and the analysis carried out exactly as described in our previous paper.¹ From the amount of iodine consumed the amount of hydrastine is deduced by using the factor of the hydrastine hexaiodide, *i. e.*, 0.60403 gram of hydrastine for one of iodine consumed.

For a gravimetric estimation another portion of twenty cc. of the filtered solution is run into a separator and the hydrastine shaken out with benzene and ammonia. All the coloring-matter remains in the aqueous liquid, and a perfectly colorless solution of hydrastine in benzene is obtained. The benzene solution is then filtered through a small filter into another separator, the first separator and filter washed with benzene and the hydrastine again shaken out with water acidulated with sulphuric acid. At last from the watery solution the hydrastine is shaken out with ether and ammonia, the ether poured into a tared beaker and slowly evaporated in a dark place. After drying in a vacuum over sulphuric acid and paraffin the beaker is weighed. The hydrastine is left in perfectly white crystals, and only a slightly yellowish tint can be seen on the sides of the beaker. This tint is probably due to traces of canadine, which becomes yellow² on exposure to the light. Of course instead of shaking out, the method of perforation may be used if preferred.

¹ This Journal, 20, 722 (1898).

² E. Schmidt: *Arch. d. Pharm.*, 232, 141 (1899).

For the estimation of berberine a current of dry air is passed through the Soxhlet till all the ether is removed, the Soxhlet connected with an Erlenmeyer containing forty or fifty cc. of alcohol, and the extraction continued until the alcohol comes out colorless. The alcoholic extract containing the berberine, and considerable quantities of extractive matter, is poured out into an evaporating dish, the Erlenmeyer washed out with hot water and a little dilute acetic acid, the washings added to the evaporating dish and the latter kept on a water-bath, adding water from time to time till all the alcohol has disappeared. A little more diluted acetic acid is now added, the dish covered and when completely cold its contents are filtered into an Erlenmeyer having the capacity of about three or four hundred cc.¹

Six to eight cc. of acetone are added to the contents of the Erlenmeyer, to which the washings of the dish and the filter have been added, and then a ten per cent. solution of sodium hydroxide is added, drop by drop, till the precipitate first formed ceases to disappear on shaking, and the liquid acquires a strongly alkaline reaction. The Erlenmeyer is then stoppered and shaken in a circular direction for about ten or fifteen minutes, and then set aside in a cool place for two or three hours. The berberine-acetone separates out in crystals, some of which adhere to the sides of the vessel. The supernatant liquid is then poured on a small filter, the precipitate washed once or twice by decantation and then on the filter till the washings are colorless. The filter is then pierced and, by means of the wash-bottle, the precipitate is returned to the same Erlenmeyer in which the precipitation took place. In this way all loss is avoided. To the precipitate about four or five cc. of a five per cent. solution of sulphuric acid is now added and then water enough to make about one or two hundred cc. The Erlenmeyer is now put into hot water when the precipitate will completely dissolve in the course of a few minutes. The solution is now poured out into a long-necked flask, washing the Erlenmeyer several times, the

¹ In the remaining procedure, the simplest way would be to precipitate the berberine with hydrochloric or nitric acid, but in this case a considerable amount of extractive matter contaminates the precipitate and too high a yield would result though the error in this respect might be compensated to some extent by the solubility of the hydrochloride or nitrate in water. But the best way is to purify the berberine by converting it into berberine-acetone, regenerate the alkaloid by means of sulphuric acid and then estimate it volumetrically by standard potassium iodide.

flask put on an asbestos plate and kept very gently boiling for about an hour and a half or two hours, adding hot water from time to time if necessary.

The flask is now cooled and its contents poured out into a liter measuring flask¹ into which there has been previously taken from a burette one hundred cc. of twentieth normal potassium iodide. The flask is washed several times, the washings added to the measuring flask and the latter filled up to one liter and set aside over night. Five hundred cc. are now filtered off into another liter flask, fifty cc. of twentieth normal silver nitrate, and nitric acid, added to the flask, which is filled up to one liter, well shaken, filtered, and five hundred cc. of the filtered liquid titrated back with fortieth-normal ammonium thiocyanate, using ferric alum as indicator. Twice the number of cubic centimeters of the thiocyanate solution used is equal to the number of cubic centimeters of the potassium iodide solution consumed by the berberine, representing ten grams of the Hydrastis root. By multiplying the number of cubic centimeters of twentieth normal potassium iodide consumed, by 0.167125, the percentage of anhydrous berberine in the root is obtained, as one cc. of the potassium iodide solution is equal to 0.0167125 gram of berberine.

In our assay of Hydrastis Canadensis three samples of powdered Hydrastis were treated in the way described. The berberine was estimated volumetrically, the hydrastine both iodometrically and gravimetrically.

FOR HYDRASTINE.

	Iodine consumed by two grams of the root.	Hydrastine.	
		Iodometric.	Gravimetric.
1	0.0760015	2.29	2.29
2	0.0772012	2.33	2.30
3	0.0777770	2.35	2.28

FOR BERBERINE.

	Number of cc. of twentieth normal KI consumed by ten grams of the root.	Berberine, anhydrous.
1	15.1	2.52
2	15.3	2.55
3	14.8	2.47

With regard to the precipitation of berberine by potassium

¹ The berberine hydriodide being extremely bulky the error arising from the space occupied by the precipitate is reduced to a minimum by using a large flask.

iodide we wish to draw attention to the fact that even a solution of the free alkaloid without any addition of acid is precipitated by potassium iodide. As there is no acid to combine with the potassium the question is, what becomes of the metal when the iodine of the potassium iodide is taken up by the berberine? That there is no potassium in the precipitated berberine hydriodide was proved by igniting the precipitate with sulphuric acid and ammonium nitrate, when no trace of residue was to be found. All the potassium must then pass into the filtrate and part of it must exist there as a salt of something acting as an acid, as there is no trace of alkalinity in the filtrate. No one of the indicators gives an alkaline reaction. We acidulated the filtrate with sulphuric acid, shook it up with ether, washed the ether till there was no reaction given for iodine by sodium nitrite and starch, nor for sulphates by barium chloride, and evaporated the ether to dryness; a very small amount of a crystalline substance was left, which would seem to indicate the presence of an organic acid, but the quantity was too small for a closer examination. We intend to take a larger quantity of pure berberine into operation and investigate the subject thoroughly in the near future.

UNIVERSITY OF MICHIGAN,

April, 1899.

UPON THE ACTION OF DIAZO COMPOUNDS ON THYMOLPARASULPHO ACID.

[SECOND PAPER.]

BY JAMES H. STEBBINS, JR.

Received May 16, 1899.

IN my former paper¹ I described several azo compounds obtained by combining diazobenzene chloride, diazopara-toluene chloride, and diazoxylene chloride with thymolparasulpho acid.

Contrary to precedent, it was observed that the three compounds named, notwithstanding their increasing molecular weight, were all possessed of about the same yellow color, and were all three more or less unstable, being partially decomposed by boiling water.

It therefore seemed of interest to ascertain in what manner the

¹ This Journal, 3, 112.

sulpho acids of higher diazotized amines would behave towards thymolparasulpho acid. With this end in view, the following experiment was made:

ACTION OF NAPHTHIONIC ACID ON THYMOLPARASULPHO
ACID.

One twenty-eighth mol. of eighty-three per cent. sodium naphthionate, or 10.4 grams, were dissolved in 200 cc. of water, and to it were added one twenty-eighth of two mols. of hydrochloric acid of 1.20 sp. gr., or six and four-tenths grams. Furthermore one twenty-eighth mol. of seventy-nine per cent. sodium sulphite (NaNO_3) or two and nine-tenths grams were dissolved in fifty cc. of water, and the solution thus obtained was gradually stirred into the naphthionate solution.

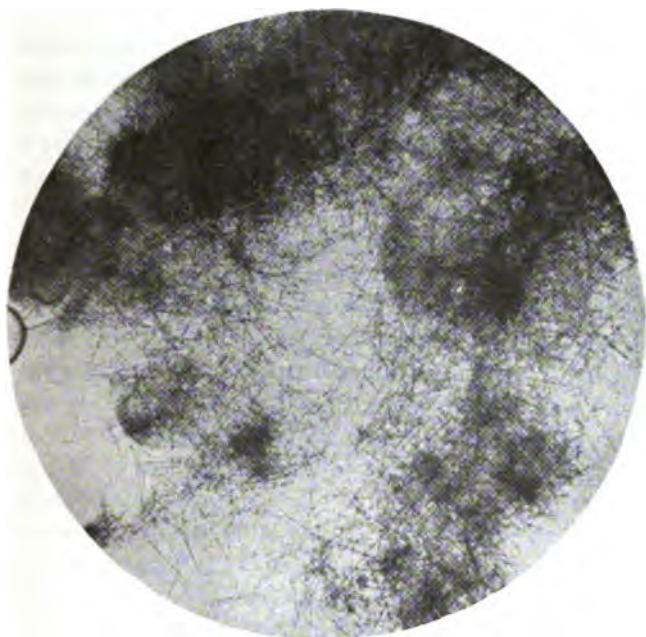
The diazonaphthionic acid thus formed, was then slowly run, under constant stirring, into a cooled solution of one-twenty-eighth mol. thymolparasulpho acid, or eight and two-tenths grams, dissolved in 100 cc. of water made alkaline with four and three-tenths grams of caustic soda.

The mixture at first turns bright red, but gradually increases in depth of color, as the diazo solution is run in, till at last the solution assumes a deep red-brown color, tinged with a suspicion of crimson, which latter color becomes all the more manifest if a drop of the solution be placed upon filter-paper. This phenomenon would suggest a mixture of two colors; *viz.*, a brown and a crimson color.

Some foam is formed during the operation, but whether this is due to an evolution of nitrogen, or to the presence of carbonates in the caustic soda used, I am at present unable to say. The reaction mixture was allowed to stand over night and was then heated to boiling, and saturated with dry sodium chloride.

A reddish brown precipitate A is thus thrown down, and was collected upon a filter and dried.

The filtrate B contains a crimson-red dye-stuff which is so exceedingly soluble in water that it was found next to impossible to precipitate it with salt. A small quantity, however, was obtained by saturating the filtrate at a boil with a large excess of salt, and filtering from the brownish red precipitate formed. Even after this treatment a considerable quantity of the coloring-matter remains in solution. It may, however, be precipitated



Ba-Salt Naphthionic Acid Azothymolparasulpho Acid.

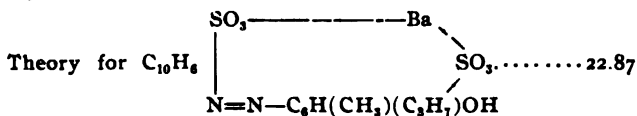
with barium chloride as a barium salt, but the yield was so small that an examination of the product had to be abandoned for the present.

Brown Precipitate A.—The brown product precipitated with salt, and alluded to above, was dissolved in water, filtered, and treated with an excess of barium chloride. A copious yellow-brown precipitate C of a barium salt was thrown down. This was collected upon a filter, and washed with cold water until free from all excess of barium chloride, and then dried. The filtrate from this barium salt contains a purplish red dye-stuff in solution, which seems to be identical in color with the dye-stuff contained in filtrate B. From this it would therefore seem, that two coloring-matters are formed by the action of diazonaphthionic acid on thymolparasulpho acid, one of which is brownish, and easily precipitable by sodium chloride or barium chloride, and the other purplish red to crimson, and so very soluble in water that it is only precipitated therefrom with great difficulty by either sodium chloride or barium chloride. The latter is, however, only formed in very small quantity, and its great solubility in water would indicate that it contains more than two sulpho groups. It is therefore possible that it owes its formation to the presence of a small quantity of thymoldisulpho acid, in the thymolparasulpho used.

The barium salt C, in a moist condition, is fairly soluble in boiling water, but once dried its solubility is greatly diminished. It is slightly soluble in boiling ninety-five per cent. alcohol, but readily soluble in proof spirit. It may be obtained in a crystalline form, by dissolving it in boiling water, and allowing it to cool slowly. It is thus obtained as a perfect network of orange-colored hair-fine needles. (See plate.)

BARIUM ESTIMATION.

	Gram.
Substance taken	0.5379
Barium sulphate found	0.1939
	Per cent.
Equivalent to barium	24.43

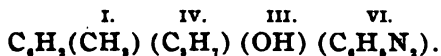


It is therefore probable that the compound under examination is represented by the above formula.

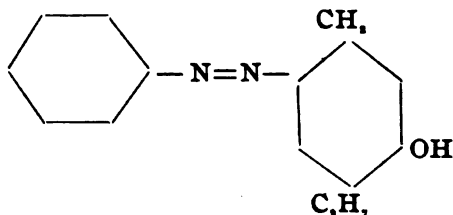
G. Mazzara and G. Posseto¹ on treating thymol in alkaline solution with diazobenzene chloride obtained a mixture of monophenylazothymol, $C_6H_5-N_2-C_6H_4(CH_3)(C_6H_5)-OH$ and monophenyldisazothymol $(C_6H_5N_2)_2C_6H(CH_3)(C_6H_5)(OH)$.

The former of these two products on reduction with tin and hydrochloric acid, and then oxidation of the reduction product with ferric chloride, gave a thymoquinone melting at 45° , while the diazo product by the same treatment, gave an oxythymoquinone melting at $167^\circ-169^\circ$.

From this they conclude that the phenylazothymol obtained has the following constitution:

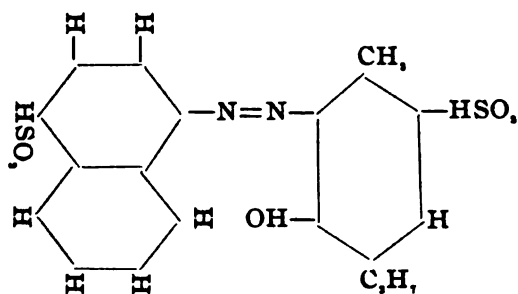


The above expressed graphically would give us the following:

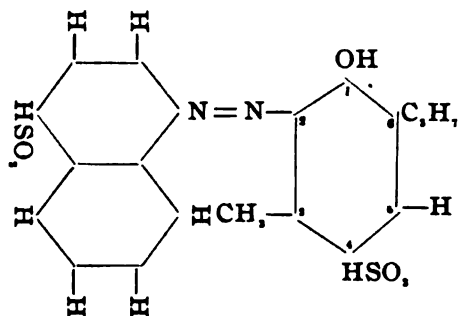


If we now consider the naphthionic acid azothymolparasulpho acid, $C_{10}H_7N_2C_6H(CH_3)(C_6H_5)(OH)HSO_3$, above alluded to, and produced by the action of diazonaphthionic acid, on thymolparasulpho acid, it will be seen that as the sulpho group in the thymol ring, occupies the para position with relation to the OH group, there are only two other positions for the diazo group to enter; *viz.*, the ortho and the meta positions, but from the general rules governing the formation of azo compounds, it is evident that the diazo group must enter the ortho position with relation to the OH group, and hence the constitution of this compound may probably be represented as follows:

¹ *Gazz. chim. ital.*, 18, 52.



Or using a somewhat less antiquated formula for thymolpara-sulpho acid, we would get



It will therefore be seen from the foregoing, that the union of thymolparasulpho acid with diazo compounds of the naphthalene series, produces brownish, to crimson coloring-matters, in contradistinction to those obtained with the diazo compounds of the benzene series.

A parallel test made with diazobetanaphthalenesulpho acid (Casella's acid), and sodium thymolparasulphonate has shown that here'too a reddish brown coloring-matter is formed.

It was intended at the beginning of this investigation, to go into the matter more at length, but circumstances which I had not foreseen have forced me to suspend my work, and to present it in its present unfinished condition.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

A NEW VOLUMETRIC METHOD FOR MAGNESIUM.¹

BY RICHARD K. MEADE.

Received June 5, 1899.

ONE of the elements for which, so far, no satisfactory volumetric method of determination, of general application, has been found, is magnesium. Stolba² suggested a volumetric method depending upon the fact that one molecule of magnesium ammonium phosphate required two molecules of mineral acid for solution. Hart and Sutton both describe the method in detail, in their works upon volumetric analysis, and call attention to its accuracy. Hartzell, a student in the laboratory of Lafayette College, in his thesis work for graduation, in 1897, made use of the method in determining magnesia in cement and the result of his investigations, also, showed the method to be fairly accurate. The great objection to Stolba's method, particularly if it is resorted to as a time-saver, is the tedious washing of the precipitated magnesia with alcohol, in order to get rid of the ammonia, making the volumetric determination very little if any quicker than the gravimetric. In any event, so far as I know, the method is very little if ever used even in commercial laboratories where magnesia determinations are a part of the daily routine. .

Analogous to the phosphates are the arsenates. If instead of adding sodium phosphate to an ammoniacal solution containing magnesium we add sodium arsenate, magnesium ammonium arsenate, corresponding to magnesium ammonium phosphate, is precipitated. This reaction is of course a familiar one, since it is the one upon which the usual gravimetric determination of arsenic is based. Now if the magnesium in a solution can be entirely precipitated as a double arsenate of magnesium and ammonium, if the magnesium and arsenic in this compound bear a fixed ratio to each other, if the precipitate can be collected and washed free from sodium arsenate, then clearly any volumetric method which will give us the weight of arsenic in the precipitate

¹ Read before the Lehigh Valley Section of the American Chemical Society, May 16, 1899.

² *Chem. Centrbl.* (1866), 728.

will also tell us indirectly the amount of magnesium in the solution. From the formula of the double salt, $\text{Mg}_2(\text{NH}_4)_2\text{As}_2\text{O}_7 + \text{H}_2\text{O}$, it will be seen that one atom of magnesium is equivalent to one atom of arsenic and consequently the ratio between the magnesium and arsenic is 24.28 : 75.01.

As the first step looking to the formulation of a volumetric method along these lines, a stock solution of magnesium was prepared as follows: Fifty grams of pure magnesium chloride were dissolved in about 700 cc. of water and a little ammonium oxalate added to precipitate any traces of calcium present. The solution was allowed to stand for a day when the very slight precipitate of calcium oxalate was filtered off. A sufficient quantity of ammonium oxalate to convert all the magnesium in the solution to magnesium oxalate was next added and the solution evaporated to small bulk over a water-bath. The separated magnesium oxalate was collected, washed, dried, and ignited, first at a low temperature and then at a higher until finally at a red heat. Of the pure magnesium thus obtained, five grams were dissolved in dilute hydrochloric acid and the solution diluted to two liters. Each fifty cc. of this solution should have been equivalent to 0.2500 gram of magnesium oxide. Checked by precipitation with sodium phosphate, fifty cc. gave:

I. 0.6900 gram of $\text{Mg}_3\text{P}_2\text{O}_8$ equivalent to 0.2497 gram of MgO .

II. 0.6891 gram of $\text{Mg}_3\text{P}_2\text{O}_8$ equivalent to 0.2493 gram of MgO .

Checked by evaporation to dryness and ignition of the residue, fifty cc. gave:

0.2490 gram of MgO .

0.2498 gram of MgO .

The average of the four determinations is 0.2495 gram MgO .

A search into the literature on the solubility of the magnesium ammonium arsenate showed the precipitate to be less soluble where an excess of sodium arsenate was present in the ammoniacal solution; accordingly, wherever the magnesium was precipitated by sodium arsenate, a considerable excess of the precipitant was used. The precipitate of course must be washed with dilute ammonia water and, as it is not entirely insoluble in this medium, the volume of the washing fluid should be kept as small as possible.

Following these points, fifty cc. of the stock solution were diluted to 500 cc. and 50 cc. of sodium arsenate (ten per cent.) solution added; then ammonia, drop by drop, with constant stirring until the precipitate began to form. At this point the addition of ammonia was interrupted and the solution stirred for five minutes after which one sixth the volume of the solution of strong ammonia was added and the mixture stirred for five minutes longer and allowed to stand over night. In the morning the precipitated magnesium ammonium arsenate was collected in a Gooch crucible, dried, and ignited at a very low temperature and weighed as magnesium pyroarsenate, containing 25.94 per cent. of magnesium oxide. The results were:

No.	$Mg_3As_2O_7$ Gram.	Equivalent to MgO. Gram.
1	0.9599	0.2490
2	0.9545	0.2476
3	0.9592	0.2488
4	0.9573	0.2483
Average		0.2484
Instead of		0.2495
Difference		0.0009

As a further test the magnesia from fifty cc. of the stock solution was precipitated as described, dissolved in dilute hydrochloric acid and the arsenic thrown out of solution with hydrogen sulphide. The magnesium remaining, was then determined as pyrophosphate with the following results:

No.	$Mg_2P_2O_7$ Gram.	Equivalent to MgO. Gram.
1	0.6883	0.2490
2	0.6865	0.2484
3	0.6870	0.2486
Average		0.2487
Instead of		0.2495
Difference		0.0008

In the same manner, the magnesium in fifty cc. of the stock solution was precipitated as magnesium ammonium arsenate, dissolved in hydrochloric acid and the arsenic determined as magnesium pyroarsenate by addition of magnesia mixture. The results were:

No.	Mg ₃ As ₂ O ₇ . Gram.	Equivalent to MgO. Gram.
1	0.9590	0.2488
2	0.9536	0.2474
3	0.9552	0.2478
Average		0.2481
Instead of		0.2495
Difference		0.0014

These three sets of results while a little low, showing that a slight loss of magnesia is incurred, probably due to solution of the precipitate in the mother-liquor and the wash-water, nevertheless, fall well within the limits of allowable variation for technical work, and show the ratio between the magnesium and arsenic to be constant.

The next step was to find a suitable volumetric method for determining the arsenic. This being in the state of arsenic acid excluded all methods supposing the element to be in the condition of lower oxidation. The methods of Pierce and McCay depending upon the precipitation of the arsenic as silver arsenate by an excess of standard silver nitrate and the determination of, either the silver in the precipitate or the excess of silver in the solution, by titration with sodium thiocyanate were also not considered, as both time and expense made them unsuitable for commercial work.

Of the methods depending upon the reduction of the arsenic to arsenious acid and the titration of the latter by standard iodine, that making use of the reaction between arsenic acid and potassium iodide in acid solutions offered the best field for investigation and following the method as laid down by Gooch and Browning,¹ several determinations were made. The process followed consisted in dissolving the precipitated arsenate in dilute sulphuric acid, adding an excess of potassium iodide and ten cc. of sulphuric acid (1 : 1) and diluting to 100 cc. The solution was boiled rapidly until the volume reached 40 cc. and the free iodine in the solution destroyed by careful addition of sulphurous acid (roughly made about one-half normal). Sodium carbonate was then added until the solution was nearly neutral and next an excess of sodium bicarbonate over what was required to make it so. The arsenious acid was then titrated with standard iodine

¹ *Am. J. Sci.* (3), 40, 66.

solution. This latter was made by dissolving 52.24 grams of pure resublimed iodine in a solution of 75 grams of potassium iodide in 200 cc. of water and diluting to one liter. Each cubic centimeter of this solution should be equivalent to 0.005 gram of magnesium oxide. The following satisfactory results were obtained by this method.

No.	Stock solution taken. cc.	Equivalent to MgO. Gram.	Iodine required. cc.	Equivalent to MgO. Gram.
1	50	0.2495	49.6	0.2480
2	50	0.2495	49.7	0.2485
3	25	0.1247	24.9	0.1245
4	25	0.1247	24.9	0.1245
5	10	0.0499	9.9	0.0495
6	10	0.0499	10.0	0.0500

The time required to determine the arsenic by this method was from one-half to three-quarters of an hour.

The next, and the method finally adopted as the one most suited to the volumetric determination of magnesium, was the one worked out by A. Williamson and described by him in the *Journal of the Society of Dyers and Colourists*, May, 1896. A description of the method is also to be found in Sutton's "Volumetric Analysis," page 369.

It depends like the method of Gooch and Browning upon the reaction between arsenic acid and potassium iodide. Williamson found that where a solution of arsenic acid contained sufficient sulphuric or hydrochloric acid the arsenic is quickly reduced from the higher to the lower state of oxidation, even in the cold, according to the reaction



For every molecule of arsenic acid reduced, corresponding to two atoms of magnesium, two molecules or four atoms of iodine are liberated. This latter is titrated with sodium thiosulphate and from the amount of standard solution required the magnesium calculated.

The process followed consisted in dissolving the precipitated magnesium ammonium arsenate in dilute hydrochloric acid, washing the filter-paper well with the acid and, after adding potassium iodide and allowing to stand for a few minutes, titrating with standard thiosulphate. This latter corresponded, cubic

centimeter for cubic centimeter, with the iodine solution mentioned above. Below are the results.

No.	Stock solution taken. cc.	Equivalent to MgO. Gram.	"Hypo" required. cc.	Equivalent to MgO. Gram.
1	50	0.2495	49.8	0.2490
2	50	0.2495	49.9	0.2495
3	25	0.1247	25.0	0.1250
4	25	0.1247	24.9	0.1245
5	10	0.0499	9.95	0.0498
6	5	0.0249	5.0	0.0250

Determinations required only from seven to ten minutes by this method after the arsenic was in solution and were just as accurate as those by the longer method of digestion with potassium iodide.

The attempt was next made with success to hasten the precipitation of the magnesium by violent agitation. Fifty cc. of the stock solution were measured into a large Erlenmeyer flask, diluted to about 500 cc. and one-third this volume of strong ammonia and 50 cc. of a ten per cent. solution of sodium arsenate added, the flask corked up tightly and shaken violently by hand for ten minutes. After allowing the precipitate to settle, it was filtered and the arsenic determined as described above.

No.	Stock solution taken. cc.	Equivalent to MgO. Gram.	"Hypo" required. cc.	Equivalent to MgO. Gram.
1	50	0.2495	49.9	0.2495
2	50	0.2495	49.9	0.2495
3	25	0.1247	24.8	0.1240
4	15	0.0748	15.0	0.0750
5	10	0.0499	9.9	0.4950
6	5	0.0249	4.9	0.0245

The time required for the precipitation, filtration, washing, re-solution, and titration, had now been shortened to about three-quarters of an hour.

The standard thiosulphate was titrated against standard sodium arsenate, prepared by dissolving 12.29 grams of pure arsenious acid in nitric acid, evaporating to dryness on a water-bath, neutralizing with sodium carbonate and diluting to one liter. Each cc. of this solution was equivalent to 0.005 gram of magnesium oxide. The values obtained by titration of the standard thiosulphate against this solution coincided with those

obtained by titration with standard iodine solution. The values obtained by titration against standard bichromate and potassium iodide did not differ materially from those obtained by titration against standard arsenate or standard iodine.

The method finally worked out is as follows :

Pour the solution, which should not contain too great an excess of ammonium chloride or ammonium oxalate, into a large Erlenmeyer flask or a gas-bottle of sufficient capacity. Add one third the volume of the solution of strong ammonia and fifty cc. of sodium arsenate. Cork up tightly and shake vigorously for ten minutes. Allow the precipitate to settle somewhat, and wash with a mixture of three parts water and one part strong ammonia, until the washings cease to react for arsenic. Avoid using an excess of the washing fluid, however. Dissolve the precipitate in dilute hydrochloric acid (1 : 1), allowing the acid solution to run into the flask in which the precipitation was made, and wash the filter-paper with the dilute acid, until the washings and solution measure 75 or 100 cc. Cool, if not already so and add from three to five grams of potassium iodide, free from iodate ; allow the solution to stand a few minutes and then run in the standard thiosulphate until the color of the liberated iodine fades to a pale straw color. Add starch and titrate until the blue color of the iodide of starch is discharged. If preferred, an excess of thiosulphate may be added, then starch and standard iodine until the blue color is produced. On adding the iodide of potassium to the acid solution, a brown precipitate forms which, however, dissolves when the thiosulphate is added.

Below are some results upon the method as given above :

Sample.	MgO. Gravimetric. Per cent.	Thiosulphate required. cc.	MgO. Volumetric. Per cent.
Dolomite	21.78	43.3	21.65
		43.4	21.70
Limestone	9.16	18.2	9.10
		18.2	9.10
Slag	16.42	32.6	16.30
		32.5	16.25
Cement, Portland	2.57	5.1	2.55
Cement, Natural	11.03	22.0	11.00
		22.2	11.10

EASTON, PA.,

May 15, 1899.

NOTES ON ALKALI SOIL IN MONTANA.

BY F. W. TRAPHAGEN AND W. M. COBLEIGH.

Received April 24, 1899.

EVEN the most casual observer, passing through the state by rail, must have been more or less impressed by the appearance of occasional spots, barren of vegetation, and incrustated with a white, red or yellow salt, which are to be seen at various points in Montana. These are the so-called "alkali" soils, and represent the worst phase of the condition.

The agriculturist recognizes two kinds of alkali: the "white" and the "black," the former consisting mainly of sodium sulphate and the latter of sodium carbonate.

A solution of the "black" alkali, on account of its solvent action upon organic matter, dissolves the humus from the soil, and upon evaporation leaves it as a shiny black coating upon the surface, or in black concentric rings around the pools in which it collects. Vegetation is destroyed by contact with solutions of sodium carbonate, the stems, especially at the surface of the ground, being frequently completely girdled. Hilgard has found that as little as one-tenth per cent. sodium carbonate in the surface foot is deleterious.

On the other hand a much larger amount of the "white" alkali may exist without affecting vegetation injuriously. In Montana, the alkali consists almost entirely of sulphates and rarely possesses a strong alkaline reaction. I have found crops thriving in the presence of as much as six-tenths per cent. of the "white" alkali. The "white" alkali seems to produce its injurious effects when present in excess, not through any chemical influence, but rather by interference with the process of osmosis by which the plant obtains its mineral food and water, the external solutions frequently becoming of much greater density than the sap.

The following analyses of typical alkali soils of the Yellowstone Valley, will give an idea of the salts usually present and their relative proportions.

Sample No. 372, from Hesper Farm, uncultivated portion, taken at fourteenth foot in depth, about the center of "zone of

concentration." The figures give actual percentage of constituents soluble in water.

SAMPLE NO. 372, HESPER FARM.

	Per cent.
Soluble silica.....	0.004
Calcium sulphate	0.150
Magnesium sulphate	0.130
Potassium sulphate.....	0.009
Sodium sulphate	0.320
Sodium nitrate	0.018
Alkalinity in terms of sodium carbonate.....	0.096

SAMPLE NO. 304, SURFACE CRUST.

	Per cent.
Soluble silica.....	0.054
Calcium sulphate.....	1.28
Magesium sulphate.....	14.91
Potassium sulphate.....	0.83
Sodium sulphate	26.65
Sodium nitrate.....	trace
Sodium chloride.....	0.637
Alkalinity in terms of sodium carbonate.....	0.144

SAMPLE NO. 405, SURFACE CRUST.

	Per cent.
Soluble silica.....	0.035
Calcium sulphate.....	1.38
Magnesium sulphate	3.21
Potassium sulphate	0.18
Sodium sulphate	6.43
Sodium nitrate	0.091
Sodium chloride.....	0.578
Alkalinity in terms of sodium carbonate.....	0.048

It will be seen that the actual percentage of soluble matter present varies very greatly, but the ratios of the quantities of the different salts is remarkably constant.

All regions of deficient rain-fall are subject to the accumulation of soluble salts in their soils, for, unlike humid sections, there is an insufficient quantity of water to carry off the salts rendered soluble by the natural processes of rock-disintegration.

Add to this the presence of rocks of marine origin which have been deposited in the presence of sulphates and chlorides, and you have a fruitful source of soluble alkali salts.

Analyses of the Fort Benton shales, bordering the Yellowstone

Valley, show the presence of considerable quantities of soluble sulphates. The percentages calculated to sodium sulphate range from 1.03 to 2.02. As these rocks, by their decomposition, contributed very largely to the formation of the soils of the Valley, the source of the "alkali" is readily apparent.

Where the soil exists in its virgin condition, undisturbed by plow or irrigation, the alkali is present at a considerable depth, being practically all concentrated in a particular zone. The series cited below was obtained from a point above the line of the ditch, and in consequence had never been irrigated, and further because of this no attempts at cultivation had ever been made.

SAMPLES FROM UNCULTIVATED PORTION OF HESPER FARM.

Lab. No.	Depth in inches.	Sodium sulphate. Per cent.	Alkalinity in terms of	Moisture. Per cent.
			sodium carbonate. Per cent.	
359	0- 12	0.016	0.025	3.40
360	12- 24	0.006	0.021	4.30
361	24- 36	Trace	0.032	3.50
362	36- 48	0.015	0.021	3.50
363	48- 60	0.045	0.017
364	60- 72	0.077	0.014
365	72- 84	0.094	0.021
366	84- 96	0.123	0.014	.. .
367	96-108	0.104	0.014
368	108-120	0.115	0.025
369	132-144	0.288	0.021
370	144-156	0.379	0.017
371	156-168	0.737	0.010
372	168-180	0.780	0.017
373	180-192	0.745	0.014
374	192-204	0.605	0.017
375	204-216	0.574	0.014
376	216-228	0.458	0.010

With the advent of irrigation, the salts, usually deeply located, begin to rise to the surface. The water table formerly many feet deep approaches nearer and nearer to the surface, and of course brings the soluble salts with it.

An example illustrating the rise of the ground water may not be out of place here. In 1882, Mr. Hiram Abshire, whose ranche is near the middle of the valley, dug a well finding water at a depth of thirty-one feet; in September, 1897, fifteen years

later, the water had risen to within six feet of the surface. This is but one of many similar cases.

Samples taken from fields located on opposite sides of the main ditch show the zone of concentration of the soluble salts to be considerably deeper above the ditch than below it, and this is true even though the fields have never been irrigated.

Irrigation has the effect of concentrating the salts at the surface, for of course that which the water dissolves in its downward course, is brought up by it again when it rises by capillary action to supply surface losses due to evaporation. When it in turn evaporates, its salts are left upon the surface.

The following examples illustrate strikingly this action :

ALFALFA FIELD, IRRIGATED, FAIR CROP.

Lab. No.	Depth in inches.	Sodium sulphate. Per cent.	Alkalinity in terms of sodium carbonate Per cent.
221	0-12	0.140	0.017
222	12-24	0.198	0.014
223	24-36	0.039	0.014
224	36-57	0.036	0.014
225	57-72	0.036	0.017
226	72-90	0.039	0.017

BLUE JOINT FIELD, UNIRRIGATED, USED FOR PASTURE. ACROSS ROAD
FROM PREVIOUS LOCALITY.

Lab. No.	Depth in inches.	Sodium sulphate. Per cent.	Alkalinity in terms of sodium carbonate. Per cent.
228	0-12	0.043	0.017
229	12-24	0.063	Trace
230	24-36	0.130	0.017
231	36-57	0.150	0.010
232	57-72	0.160	0.017
233	72-90	0.166	0.017

An inspection of these tables will show that while there is more soluble matter in the unirrigated field than in the other, yet the relative amount in the upper portion of the soil is much greater in the irrigated field. In these two cases the field under irrigation, presumably at the outset identical with the other, has concentrated in the first twenty-four inches seven-tenths of the total soluble sodium sulphate contained within the soil to a depth of ninety inches; the samples from the unirrigated field show the presence of but fifteen per cent. of sulphate in the first

two feet of soil, when compared with the quantity present to a depth of ninety inches. The lesser total quantity of sulphate present is to be attributed to the influence of large crops of alfalfa, which must remove with other mineral matter large quantities of alkali salts. This influence is especially marked in the case of the alfalfa field of the Hesper Farm, where two hundred and fifty acres yield twelve hundred tons of alfalfa hay annually.

Within a few feet of this field, on the east, is a field completely destroyed by "alkali," yet not only is the alfalfa field yielding immense crops, but it bids fair to continue to do so as indicated by the low percentage of alkali salts in the soil as shown in the following section :

HESPER FARM, ALFALFA FIELD.

Lab. No.	Depth in inches.	Alkalinity in terms of		Water. Per cent.
		Sodium sulphate. Per cent.	Sodium carbonate. Per cent.	
377	0-12	0.012	0.017	11.50
378	12-24	0.004	0.021	11.70
379	24-36	0.015	0.028	12.60
380	36-48	0.013	0.025
381	48-60	0.013	0.025	19.00
382	60-72	0.019	0.039
383	72-84	0.031	0.039	19.50
384	84-96	0.054	0.032
	Water.			

Where the soil is underlain with gravel, thus affording natural underdrainage, the alkali does not rise to the surface.

This condition exists with a number of ranches in the valley, and these are singularly free from alkali.

The best method for combating the evil would appear to be underdrainage, but land is so cheap that the expense of such a remedy could not be met. Careful surface flooding, economical use of water and intelligent cropping, are the remedies in the hands of the farmer, and properly employed will solve the problem.

THE MONTANA EXPERIMENT STATION,
BOZEMAN, MONTANA.

A CHEMICAL STUDY OF WHEAT.

BY G. B. FRANKFORTER AND E. P. HARDING.

Received May 1, 1899.

WHEAT, from its great commercial importance, has been made the subject of a large number of chemical discussions. As a result of these investigations, much has been learned concerning its chemical composition, and several hitherto new substances have been described. The extreme difficulty, however, in obtaining these new compounds, together with their non-crystallinity, leaves some doubt as to the actual existence of some of them.

One of the objects which presented itself, in beginning this paper, was to verify, if possible, the existence of tritisealin and cerealin¹ and, if present, to isolate them. While the desire still exists, the numerous and perhaps less formidable questions which arose as the work progressed, led us somewhat from the original aim.

From an approximate analytical standpoint, wheat has been repeatedly examined. Konig² has made an exhaustive examination of the European varieties, while Richardson³ has carefully examined those of our own states and Canada. Throughout the whole of these analyses, only water, oil, carbohydrates, albuminoids and ash were estimated, together with the weight of the average wheat grain.

From over two hundred analyses, Richardson obtained the following averages:

	Water.	Oil.	Carbohydrates.	Fiber.	Albuminoids.	Ash.
Per cent.	10.27	2.16	71.98	1.80	11.95	1.84

The average weight of 100 grains was 3.638 grams.

WHEAT OIL.

As above indicated, the quantity of oil in wheat has often been determined; but so far as we have been able to find, the oil itself has not been thoroughly studied. At the time of the beginning of this paper, the enormous quantities of wheat germ from the great mills of Minneapolis, had little or no value. It seemed important, therefore, that some commercial value should be found for this part of the wheat. As is well known, the germ

¹ *Compt. rend.*, 37, 775; 38, 505; 42, 1122; 48, 431.

² *Nahrungs und Genussmittel.*

³ *Am. Chem. J.*, 6, 302.

of the wheat contains a very large per cent. of the oil, which was, therefore, obtained from that source.

Notwithstanding the fact that the oil has been determined in the germ and bran of the mills of Minneapolis, the improved methods of milling made it of interest to repeat some of these determinations. According to these analyses,¹ the germ was divided into three distinct parts, varying materially in the amount of oil they contain. The following per cents. of oil were obtained :

	Per cent. of oil.
First germ	9.35
Second germ	15.6
Third germ	13.75

According to the best milling authorities here, no such distinction can be made at the present time. Several analyses of all the different samples which could be obtained, ran between eleven and twelve per cent. of oil. The average of all these analyses was 11.6 per cent.

In the separation of the oil from the germ, several methods were tried. The simple extraction with ether was finally adopted as giving best results. The oil, when first extracted from the germ, has a golden-yellow color and a characteristic odor of freshly ground wheat. It has a specific gravity of 0.9292 at 15° C., and 0.9374 at 0° C. At 15°, it begins to change in appearance, becoming milky, and at 0° it becomes a cloudy semisolid. Warmed at 100° C., the above-mentioned odor is very pronounced and the oil changes color, becoming reddish brown. It is very soluble in ether, petroleum ether, chloroform, carbon disulphide, acetone and comparatively so in methyl and ethyl alcohols. It cannot be regarded as a drying oil, as it loses slightly in weight after exposure to the air for a month. After that time, the weight appears perfectly constant. The following table will show that the oil can not even be regarded as a semi-drying oil. For the sake of comparison, duplicate drying experiments were made with pure linseed oil.

GAIN (+) AND LOSS (—) IN PARTS PER HUNDRED AFTER
DRYING AT THE ORDINARY TEMPERATURE THE INDICATED NUMBER OF DAYS.

	Number of days.						
	5	10	15	20	25	30	35
Linseed oil	0.037	0.13	0.28	1.74	4.82	7.55	7.94
Wheat oil	0.037	0.077	0.15	0.24	0.30	0.37	0.37

¹ *Am. Chem. J.*, 6, 398.

	Number of days.							
	40	45	50	55	60	65	70	75
Linseed oil	7.94	7.94	7.90	7.90	7.90	7.95	7.95	8.43
Wheat oil	0.41	0.42	-0.22	-0.26	-0.28	-0.28	-0.30	-0.42

The variation in the results between thirty-five and fifty days is undoubtedly due to outside physical conditions. Under exactly the same temperature, linseed oil will more than likely increase in weight uniformly, until the maximum of 8.5 per cent. is reached. Wheat oil, as indicated in the above table, can not even be regarded as a semidrying oil. Although a slight increase in weight was indicated during the first forty-five days, the loss by weight which followed, a little more than counterbalanced the gain. The oil, at the end of the above-stated time, appeared almost unchanged.

VISCOSITY OF WHEAT OIL.

The viscosity of wheat oil was taken at the various temperatures indicated below, as compared with pure rape oil. The following is a ratio between the two oils:

Temperature	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
Wheat oil	1.43	1.81	2.57	1.92	1.67	1.48	1.40	1.39	1.27	1.20	1.14

While rape oil, which was taken as unity, was found to vary quite uniformly with increase of temperature, wheat oil increased more rapidly from 0° to 20° than from 20° to 100° C., making the maximum ratio between the two oils at 20° C. This ratio may be represented by the following curve in which the temperature is the abscissa, and the relative viscosity, the ordinate :

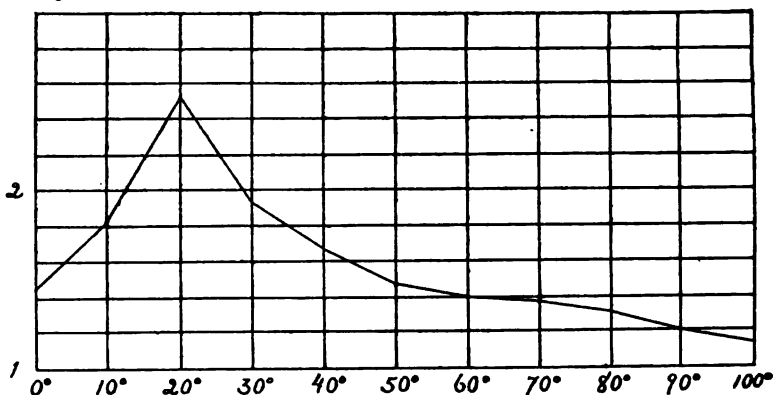


Fig. 1.—Viscosity Curve of Wheat Oil, Rape Oil as Unity.

INDEX OF REFRACTION.

The index of refraction of wheat oil was taken at different temperatures by the Pulfrich refractometer. The following is a comparison of wheat oil with corn and linseed oils:

Temperature	20°	30°	40°	50°	60°	70°	80°
Corrected index of wheat oil	1.47878	1.47544	1.47181	1.46858	1.46459	1.46161	1.4586
Corn oil	1.47789	1.47436	1.47053	1.46728	1.46360	1.46002	1.45642
Linseed oil	1.48558	1.48072	1.47730	1.47329	1.46954	1.46697	1.46281

The above readings were taken with wheat oil, just as it was obtained from the germ, by extracting with ether. The oil, therefore, contained all the substances occurring in the germ, which are soluble in ether. Some of these, it was found, could be removed by redissolving in ether and evaporating rapidly, while nearly all of these substances, including the paracholesterol, were removed by treating with alcohol. The oil thus purified had changed its properties slightly. The refractive index had changed somewhat, giving at a temperature of 20°, 30°, and 40° C., corrected indices of 1.48325, 1.47936, and 1.47447 respectively.

THE ABSORPTION SPECTRUM OF WHEAT OIL.

So far as we can learn, very little has been done on the absorption spectra of the oils. Several attempts have been made to classify the oils with regard to their absorption bands, but as these bands are in many cases due to impurities in the oil, the classification is a rather imperfect one. According to Vogel,¹ who briefly studied a few of the organic substances, these bands are nearly always due to the presence of foreign matter, as chlorophyl or other coloring substance, for by removing these coloring substances, the absorption bands disappear. This statement seems to be true within certain limits, in the case of the oils. A few of the oils undoubtedly owe their spectra to chlorophyl or some other coloring-matter. Many of them, however, have spectra entirely independent of foreign substances. Doumer,² in a spectral examination of some of the oils, divided them into four distinct classes which were represented by the following characteristics:

¹ Vogel's Spectralanalyse, Vol. I.

² *Analyst* (1885), 148.

Class I, oils showing bands due to chlorophyl.

Class II, oils without absorption bands.

Class III, oils absorbing the chemical rays of the spectrum, the red, orange, yellow and a part of the green remaining unchanged.

Class IV, oils showing absorption bands in different parts of the scale.

According to this classification, linseed, mustard and rape oils belong to Class III. A glance at the following spectra will indicate that linseed together with wheat and corn oils belong to Class IV. We have found that the spectrum depends largely upon the length of the tube used. Thus with proper length tubes these three common oils may belong to Class III, while with different tubes they may be regarded as members of Class IV. It seems evident, if this classification is to be used, that the length of the tube must be taken into consideration. Thus, wheat oil, with a 200 mm. tube, gives a rather indistinct spectrum, while with a 100 mm. tube, the spectrum is characterized by two very distinct bands, as seen below. Corn and linseed oils, with the same length tube, appear to belong to Class III. However, with a tube double the length, they undoubtedly belong to Class IV as will be seen by the following charts:

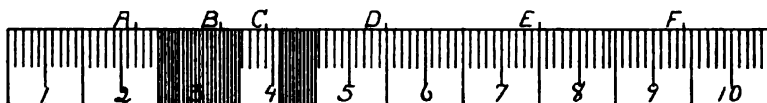


Fig. 2.—Wheat Oil.



Fig. 3.—Corn Oil.



Fig. 4.—Linseed Oil.

SOLUBILITY OF WHEAT OIL.

Solvent.	Solvent required to dissolve one gram of oil. cc.
Ether	1
Chloroform	1
Absolute Alcohol	30
Ninety per cent. alcohol	250

Some difficulties were at first experienced in determining the solubility, owing to the fact that a small quantity of unsaponifiable substance was soluble with difficulty in absolute, and almost insoluble in ninety per cent., alcohol. The oil was at first purified by dissolving in a small quantity of absolute alcohol and filtering. The tests were made on the oil thus purified.

SAPONIFICATION VALUE OF WHEAT OIL.

The saponification value of wheat oil was determined according to Köttstorfer's method which represents the number of milligrams of potassium hydroxide required to saponify one gram of the oil. The results obtained agree best with the values obtained from the semidrying oils, notwithstanding the fact that the drying experiments would not permit it to be classed in that group.

The following is the result of four determinations as compared with the results obtained from typical semidrying oils:

	Milligrams of KOH required to saponify one gram of oil.		
	Minimum.	Maximum.	Mean value.
Wheat oil	187.40	190.27	188.83
Pumpkin seed oil.....	186.6	189.81	188.21
Maize oil	188.00	193.4	190.7

In these determinations, freshly extracted oil was used, inasmuch as oil extracted for some time gave varying results.

THE IODINE VALUE.

The iodine value of wheat oil was determined according to Hübl's method. Three determinations gave the following results:

- I. 0.1998 gram of the oil absorbed 232 milligrams of iodine.
- II. 0.1866 gram of the oil absorbed 216 milligrams of iodine.
- III. 0.1505 gram of the oil absorbed 174 milligrams of iodine.

Per cent. of iodine found.			
I.	II.	III.	Average.
116.16	115.75	115.03	115.64
Pumpkin seed gave a mean of.....			121.
Maize oil gave a mean of			122.27 ¹

THE ACID VALUE.

The acid value of wheat oil was determined by the common method of titrating a known quantity of the oil with decinormal alcoholic potassium hydroxide. Three determinations gave the following results:

I. 1.594 grams of the oil required 0.066 gram of potassium hydroxide.

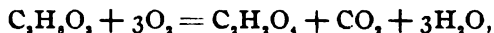
II. 1.5616 grams of the oil required 0.06284 gram of potassium hydroxide.

III. 1.268 grams of the oil required 0.05145 gram of potassium hydroxide.

	I.	II.	III.
Acid value	41.4	40.2	40.5

DETERMINATION OF GLYCEROL.

Glycerol was determined by the oxidation process, that is, the oxidation of glycerol to oxalic acids by means of alkaline potassium permanganate according to the following reaction:



and the estimation of oxalic acid, from which glycerol can be determined. The method as worked out by Benedict and Zsigmondy was used, and is briefly as follows: Two or three grams of the oil were saponified with potassium hydroxide in methyl alcohol. The alcohol was removed by evaporation, the soap dissolved in hot water and decomposed by hydrochloric acid. The whole mass was then warmed until the fatty acids had collected on the surface. These acids were filtered off and the filtrate carefully neutralized with potassium hydroxide. Ten grams of the hydroxide were now added and an excess of permanganate, or until the liquid appeared blue or dark red. The excess of permanganate was destroyed by sulphurous acid and the whole solution again filtered. The filtrate obtained was acidified with acetic acid, diluted to a liter, heated to the boiling-point, and the oxalic acid precipitated by calcium chloride.

From the calcium oxalate formed, the amount of oxalic acid and hence the per cent. of glycerol can be calculated. Five analyses gave the following results:

- I. 2.7696 grams of oil gave 0.2024 gram of glycerol.
- II. 2.9074 grams of oil gave 0.2145 gram of glycerol.
- III. 2.8778 grams of oil gave 0.2124 gram of glycerol.
- IV. 2.1640 grams of oil gave 0.1557 gram of glycerol.
- V. 3.4940 grams of oil gave 0.2631 gram of glycerol.

	I.	II.	III.	IV.	V.
Per cent. glycerol.....	7.34	7.29	7.38	7.2	7.53

DETERMINATION OF LECITHIN IN WHEAT OIL.

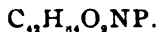
Frequent references have been made to the occurrence of lecithin in wheat, but no quantitative determinations have been made, so far as we can learn. As the base was apparently abundant in the oil, determinations were made, using the common phosphoric acid method. A known quantity of the oil was saponified with a concentrated solution of potassium hydroxide and heated on a water-bath until all the alcohol had been removed. The soap thus formed was decomposed with hydrochloric acid and the fatty acids filtered off. The filtrate, which contained all the phosphorus, was evaporated to dryness and fused with potassium hydroxide and potassium nitrate. From the fused mass the phosphoric acid was determined and the lecithin calculated. Two determinations gave the following results:

I. 23.1858 grams of oil gave 0.0697 gram magnesium pyrophosphate.

II. 27.4514 grams of oil gave 0.079 gram magnesium pyrophosphate.

	I.	II.
Calculated for lecithin	2.03	1.96

In making the above calculations, we have assumed that the lecithin was an oleyl rather than a stearyl ester. This assumption was made from the fact that in the analysis, little or no stearic acid was found in the oil. The formula used therefore, was



PARACHOLESTEROL IN WHEAT OIL.

Cholesterol was first obtained from wheat by Ritthausen.¹ By extracting the gluten, as well as the fats in wheat with ether, he obtained, on evaporating off the ether, a crystalline substance which had very similar properties to the cholesterol of Beneke.²

It was afterwards regarded as identical with an isomeric form of cholesterol discovered by Hesse,³ and called phytosterol.

In the beginning of our work on this substance, we obtained a melting-point which compared so well with phytosterol, that, with Koenig,⁴ we regarded the two substances as identical.

However, after carefully recrystallizing several times, the melting-point had risen enough to make it doubtful if the substance in wheat were phytosterol. The melting-point of phytosterol, as given by Hesse and others, is 132° – 133° C., while the purified substance from wheat, melted at 134° – 135° C. A much greater difference, however, was observed in a comparison of the wheat cholesterol with the common or animal cholesterol, the melting-point of which ranges from 140° to 148° C. These two substances, to neither of which wheat cholesterol belongs, were all which were known to the earlier authorities, and according to Maly,⁵ these two substances were identical. However, later investigations seem to prove beyond a doubt, that several different forms of cholesterol exist. Reinke and Rodewald⁶ found in protoplasm of *aethalium septicum*, a substance to which, after examination, they gave the name paracholesterol. Later, Schulze and Barbieri⁷ repeated much of the work which had previously been done, and showed that no less than five different isomeric forms of cholesterol existed, or two more than had heretofore been described. These isomeric forms, together with their melting-points and optical activities, are given in the following table:

¹ *J. prakt. Chem.*, 88, 145.

² *Ann. Chem. (Liebig)*, 122, 249.

³ *Ibid.*, 192, 175.

⁴ Koenig's *Nahrungs- und Genussmittel*, 3rd Auf., 2, 461.

⁵ *Jahresber. d. Thierchem.*, (1878), 270.

⁶ *Ann. Chem. (Liebig)*, 207, 229.

⁷ *J. prakt. Chem.*, 25, 159.

ISOMERIC FORMS OF CHOLESTEROL.

Name.	Melting-point.	Optical Activity.	Authority.
Cholesterol	145°-146°	(a) _D = -36.61	Hesse
Phytosterol	132°-133°	(a) _D = -34.2	Hesse
Paracholesterol	134°-134.5°	(a) _D = -28.88	Reinke Rodewald
Caulesterol	158°-159°	(a) _D = -49.6	Reinke Rodewald
Isocholesterol	138°-138.5°	(a) _D = + 60	Schulze

As will be seen from the above table, four of these forms of cholesterol are laevo-, while the fifth is dextrorotatory, thus affording a means of distinguishing between ischolesterol and the other members. In fact, the differences between the other members, taking into consideration the melting-points, are sufficient to readily distinguish between them. A glance at this table will enable us to identify the cholesterol in wheat as paracholesterol. The melting-points are exactly the same while the planes of rotation are almost the same, as will be seen by the comparison given below:

2.7 grams of paracholesterol gave (a)_D 28.88, melting-point 134.5°.

1.7948 grams of paracholesterol gave (a)_D 27.24, melting-point 134.5°.

1.3848 grams of wheat cholesterol gave (a)_D 26.9, melting-point 134.5°.

Taking into consideration the variation in the plane of polarization obtained by Reinke and Rodewald with different amounts of paracholesterol, the results obtained with wheat cholesterol will check exactly with paracholesterol.

DETERMINATION OF PARACHOLESTEROL.

The methods given for the extraction of these isomeric forms of cholesterol are very much the same. The method in common use is as follows: The substance containing the cholesterol is first saponified with potassium hydroxide and the cholesterol extracted by ether. The ether usually dissolves some other substances besides the cholesterol. These impurities are removed by again treating with potassium hydroxide, again extracting with ether and finally recrystallizing from alcohol. Bömer¹ avoided this tedious process of evaporation, by extracting with

¹ *Ztschr. Unters. d. Nahrungs- und Genussmittel*, (1898), 31.

ether from aqueous solution. This method was found objectionable, on account of the large quantity of ether necessary to obtain perfect extraction.

Raumer¹ used good clean beach sand after saponification, the object being to assist in both evaporation and extraction.

This method will give good results, provided the sand is clean. Juckenack and Hilger² suggest the use of sodium hydroxide instead of potassium hydroxide, and filter-paper instead of sand.

The above methods all give good results, the principal difference being in the time and material required. The method which we adopted, was that involving the saponification with alcoholic potassium hydroxide and extracting the dried soap with ether in a Soxhlet extractor. Five analyses gave the following results:

- I. 20.0000 grams of oil gave 0.5216 gram of paracholesterol.
- II. 9.3380 grams of oil gave 0.2209 gram of paracholesterol.
- III. 10.3332 grams of oil gave 0.2510 gram of paracholesterol.
- IV. 10.1314 grams of oil gave 0.2510 gram of paracholesterol.
- V. 110.3000 grams of oil gave 2.7573 grams of paracholesterol.

	I.	II.	Per cent. III.	IV.	V.
Calculated for paracholesterol.	2.6	2.37	2.43	2.46	2.49

THE ELAIDIN METHOD.

Among the new methods tried, was one which involved the elaidin reaction, and which, carefully carried out, gave fairly good results. The method of operating was as follows: About twenty grams of the oil were transferred to a tall beaker, ten grams of mercury added, then ten cc. of strong nitric acid, drop by drop. The temperature was kept between 8° and 10°, on account of the violent reaction between the mercury and the nitric acid at a higher temperature. When the mercury had quite dissolved, the beaker was gently warmed, in order to remove the excess of oxides of nitrogen. The whole mass was then treated with an excess of alcoholic potassium hydroxide, evaporated to dryness on a water-bath, and extracted with ether. On evaporating off the ether, paracholesterol was obtained in comparatively pure form. By recrystallizing from alcohol, a very pure form was obtained:

¹ *Ztschr. angew. Chem.*, (1898), 555.

² *Arch. Pharm.*, 236, 369.

Two determinations gave the following results:

I. 25.64 grams of oil gave 0.464 gram of paracholesterol.

II. 15.792 grams of oil gave 0.3474 gram of paracholesterol.

	I.	Per cent.	II.
Calculated for paracholesterol.....	1.8		2.2

Although the paracholesterol was obtained in a comparatively pure form by this method, considerable difficulty was experienced in evaporating to dryness, several hours being required. It was also observed, that when more than the above-mentioned amount of nitric acid was used, the quantity of paracholesterol was diminished. Thus with double the quantities of nitric acid and mercury only four-tenths per cent., and with three times the quantity of acid and mercury only a trace, of the paracholesterol was obtained. Just why this diminution in the quantity of paracholesterol should occur, is not definitely known. The probabilities are, however, that it forms, with the excess of nitric acid, a nitrolic acid according to the common reaction.

THE ESTIMATION OF ARSENIC IN PARIS GREEN.

BY THORN SMITH.

Received May 6, 1899.

IN selecting a method for the analysis of the common insecticide, Paris green, some difficulty was encountered in finding one suitable to the ordinary requirements of rapidity and corresponding accuracy. In fact the only methods of which record was found are as follows:

First, by direct precipitation of the arsenic as magnesium pyroarsenite by means of magnesia mixture or what would be embodied in the same method, a first separation of the sulphides of arsenic and copper, by means of hydrogen sulphide, and a consequent tedious separation of the arsenic from the copper by means of ammonium sulphide, followed by the precipitation of the arsenic as at first. This latter modification is given in the majority of text-books, which mention the subject at all. Its objection is the large amount of time consumed in the operation and the danger of loss in separating the arsenic from the copper.

The second method known as the "Pearce" or "McCay" method is perhaps just as difficult with the added objection that such small amounts of the material are permitted in the pro-

cess, that errors are sure to creep in. The Paris green is fused with sodium carbonate and potassium nitrate, extracted with water, and the sodium arsenite in the water solution oxidized to the arsenate by nitric acid. The arsenate is then precipitated by silver nitrate, volumetrically. The amount of silver precipitated is to the arsenic as 108 is to 25. This method is undoubtedly well adapted to material containing but small amounts of arsenic, but where from forty to sixty per cent. is arsenic not more than two-tenths of a gram can be handled, and even then the precipitate is so bulky that inconvenience is caused. A large amount of the silver solution is also required. Either of the above will undoubtedly give exact results in the hands of an experienced analyst, but when the attempt is made by the ordinary student, woeful results generally follow and discouragement naturally attends.

In presenting the following method I may have nothing new ; in fact it may be a well-known method but at least none of the text-books at my command nor any of the standard authorities mention it. I have taken advantage of well-known reactions, and in part have used volumetric methods given by Sutton. Owing to the variable composition of Paris green, one reaction does not fit all cases but the composition and degree of oxidation of the essential elements are the same. If a copper salt be boiled with a slight excess of sodium hydroxide, in the presence of a reducing agent, cuprous oxide is formed. Therefore, if the arsenite of copper be boiled with sodium hydroxide, cuprous oxide is formed by the reducing action of the arsenite and at the same time a portion of the arsenite is oxidized to the arsenate, in this case, sodium arsenate. The latter being soluble can be filtered from the precipitated cuprous oxide, and this solution being alkaline, can be concentrated without loss. If this concentrated solution be strongly acidified with hydrochloric acid and, while still warm, an excess of potassium iodide be added, the arsenate is wholly reduced to the arsenite. The reaction is complete in a few minutes. The acid solution now contains a large amount of free iodine which can be consumed by carefully adding a dilute solution of sodium hyposulphite, followed by the addition of sodium carbonate until the solution is neutral. An excess of the bicarbonate is then added and the

solution titrated against tenth-normal iodine, using starch as an indicator.

As finally adopted the following method is used in this laboratory :

Two grams of the Paris green are weighed out, about 100 cc. of water added, and two grams of sodium hydroxide. The solution is brought to a boil and boiling continued for a few minutes. It is then allowed to cool to room temperature and the solution made up to 250 cc. The well-shaken liquid is filtered through a dry filter and fifty cc. taken for the analysis. This portion equal to four-tenths gram is concentrated to about one-half its volume and allowed to cool to about 80° C. An equal volume of strong hydrochloric acid is then added accompanied by three grams of potassium iodide and the whole allowed to stand for ten minutes (longer is not necessary). The deep red solution is slightly diluted with water to dissolve the precipitate caused by the potassium iodide and a dilute solution of sodium hyposulphite added until the color just disappears. This solution is then made neutral by the addition of dry sodium carbonate and finally an excess of sodium bicarbonate is added. Tenth-normal iodine is dropped in and the end-reaction noted by starch solution.

I have found it easier in calculating results to use a solution of iodine such that one cc. equals 0.005 gram of arsenic trioxide, instead of the exactly tenth-normal solution, one cc. of which equals 0.00495 gram. The number of cubic centimeters of such a solution multiplied by one and one-fourth equals the per cent. of arsenic trioxide in the Paris green. Two grams are taken for the assay and four-tenths taken for the operation, owing to the fact that generally but slightly less than fifty cc. are required for the titration and thus a second filling of the burette is avoided, which would be necessary were five-tenths gram taken. Working by this method an analysis can be made in less than one hour whereas by the other methods several hours or days are required. If desired, the copper as cuprous oxide can be dissolved and titrated against potassium cyanide by standard methods. The end-reaction in the arsenic titration is sometimes difficult owing to the large amounts of foreign salts in the solution. A deep red color is produced as the titration

proceeds but the unmistakable blue can easily be seen after a few trials.

Working by this method I have obtained duplicates within 0.05 per cent. which is certainly accurate enough for all practical purposes. My results have also checked the gravimetric methods very closely.

CHEMICAL LABORATORY OF THE
UNIVERSITY OF IDAHO,
April 29, 1899.

THE DETERMINATION OF SULPHUR IN BITUMENS.¹

BY S. F. AND H. E. PECKHAM.

Received June 13, 1899.

THE paper read by Mr. E. H. Hodgson, which appeared in the November (1898) number of this Journal, was read by us with great interest. It is evidently intended to be a description of a fair comparative test of the value of the several methods used for the determination of sulphur in the different varieties of bitumen examined.

We wish to call attention to a number of unrecognized, or at any rate unmentioned conditions, which, in our opinion, rendered the results, given by Mr. Hodgson, variable, and to some extent unreliable.

Of the specimens selected for analysis, it is to be said, that the two specimens called "Trinidad Lake" and "Trinidad Lake refined" are very peculiar substances. They, in common with all other Trinidad pitch, consist of a mixture of bitumen, mineral matter, organic matter that is not bitumen, and a considerable proportion of ferric and aluminic oxides, that are combined with organic radicals to form complex salts. There are sound reasons for believing that some of the sulphur is free, some of it in combination with iron as pyrites, in an extremely minute state of division, and some of it in combination as thio-salts, in which it performs a linking rather than saturating function.

There can be no question that the action of nitric acid on this complex mixture of various substances results in the formation, not only of sulphuric oxide, but of other oxides of alumina and iron, that will almost certainly form double barium salts with sulphuric acid, that are nearly or quite as insoluble as pure ba-

¹ Read at the June Meeting of the New York Section.

rium sulphate, and consequently follow, or accompany the barium sulphate, even to the final weighing.

Many years ago one of us precipitated alumina as a double barium and aluminum sulphate, from a solution of potash alum. The potash alum had been mixed, dry with barium chloride, and, as is remembered, with the potash alum largely in excess, as a puzzling problem in qualitative analysis. On attempting to dissolve the mixed salts, a barium alum or double sulphate of barium and aluminum remained undissolved. This reaction indicates why it is of importance that the oxides of iron and alumina should be removed from the solution before the barium chloride is added.

The specimen denominated "Trinidad crude" and further described as "crude asphalt from Hadley's diggings, about one mile from Trinidad Lake; it is known as 'iron pitch,' being the hardest asphalt found in Trinidad," is not asphalt at all, but is a residue from the natural distillation of the pitch by jungle fires. It is found in small masses, and in small quantity, all over the deposit, both within and without the lake, and is uniformly rejected as rubbish. It has been subjected to such a temperature that all of the water has been expelled, and the whole mass melted and brought to a condition of semifluidity. Apparently the sulphur is in part expelled, and that which remains is evidently brought into such a condition that the nitric acid process fails to produce the reaction essential to the formation of double salts, as the results of the analyses by the four processes used by Mr. Hodgson are essentially alike. The results obtained from Cuban, Alcatraz, and California asphaltum are evidently subject to the same criticism as the Lake pitches, in a less degree.

The deflagration method, as described in Mr. Hodgson's paper, is not the method used by the authors. We never used a porcelain crucible; first, for reason of its form, and second, for reason that the fluxes used will react with the porcelain, making it impossible to determine the iron, alumina, and silica in the assay.

We have modified to a slight degree our method of procedure, as experience has suggested, until finally we have weighed out such an amount of the assay as will represent about five-tenths gram of bitumen. This is very thoroughly mixed with fifteen grams each of pure and dry sodium carbonate and potassium

nitrate. The salts are first thoroughly pulverized and mixed in an unglazed porcelain mortar. Two-thirds of the mixture are then removed to a sheet of glazed paper. The assay is then mixed in the mortar with the flux in the most thorough manner and then removed to a second sheet of glazed paper. The mortar is then carefully rinsed with the remaining flux in two successive portions. The whole of the flux and assay are then brought to a uniform mixture on the glazed paper. The mixture is then placed, small portions at a time, into a two-ounce platinum crucible, heated to dull redness. No fusion with a blast-lamp is necessary, as the assay is in quiet fusion when the last portion has deflagrated. A large excess of flux lessens the violence of the combustion and also lessens the liability to loss by spattering.

The contents of the crucible are then dissolved by allowing it to remain covered with water in a beaker, preferably over night. When the solution is complete, the crucible is washed off and the contents of the beaker rendered acid with hydrochloric acid. The solution is then evaporated to dryness over a water-bath, the silica dehydrated, moistened with hydrochloric acid, treated with water and the silica filtered off, ignited, and weighed. The solution is rendered alkaline with ammonia, boiled until the excess of ammonia is removed, and the precipitate of iron and alumina dried and weighed as usual. The iron may be found in another portion with potassium permanganate and the alumina determined by difference. Lime may be determined as oxalate if desired.

The solution, freed from silica, iron, alumina, and lime, is brought to a boil, acidulated with hydrochloric acid, and the sulphuric acid precipitated with barium chloride, added in small portions at a time from a pipette. This method for the determination of sulphur is susceptible of great accuracy, if *conducted with care*. It requires great care from the beginning to the end. Mr. Hodgson's results do not indicate great care,—they are not sufficiently concordant.

We have not found the slightest difficulty in bringing out concordant results to the second place of decimals, and sometimes to the third. The method has also been proved presumably correct, by reason of determinations made by first estimating the

sulphur in a very pure asphalt and then in the same asphalt to which a weighed quantity of pure sulphur had been added dry. The results showed the amount of sulphur in the pure bitumen plus the amount of pure sulphur added.

Dr. William C. Day, of Swarthmore College, has lately used this method for determining sulphur in the natural and artificial gilsonites that he has had under examination. He has kindly given me the results that he has obtained in several analyses of these substances, which fully illustrate of what the method is capable in skilful and sympathetic hands. We give his results below.

UTAH GILSONITE.

	Weight taken. Grams.	BaSO ₄ obtained. Gram.	Sulphur. Per cent.
I	2.7111	0.0474	0.0024
II	2.1651	0.0390	0.0025
III	2.1017	0.0388	0.0027

FISH AND WOOD ASPHALT.

I	2.0218	0.0136	0.0009
II	1.9988	0.0114	0.0008

WOOD ASPHALT.

I	1.9753	0.0134	0.0009
II	1.3777	0.0095	0.0009

FISH ASPHALT.

I	2.0402	0.0287	0.0019
II	1.9954	0.0276	0.0019

INDIAN TERRITORY ASPHALT.

I	2.1676	0.2216	1.40
II	2.2410	0.2238	1.37

These results are sufficiently concordant for any purpose, and are given in preference to our own, although we have found no difficulty in obtaining equally satisfactory figures, both with pure bitumens and mixtures of bitumens with pure sulphur.

This method is simple, reasonably rapid, and accurate, does not require complex and expensive apparatus and, what is especially to be noted, furnishes a ready means for the determination in the same solution of other constituents of most solid bitumens, the correct estimation of which is often of the greatest importance.

It is to be further noted that in these analyses about two grams, more or less, are taken for an assay. These materials are all exceptionally low in sulphur. It is therefore necessary to take a larger portion than is usually found advisable in the use of this process, and when so much of the asphalt is burned it becomes absolutely necessary to use a larger proportion of the flux, otherwise some of the assay will escape oxidation.

Note.—In the discussion that followed the reading of this paper, it was claimed that mercaptans and similar constituents of bitumens could not be oxidized by this method. It has not yet been shown that mercaptans and similar sulphur compounds exist as constituents of crude bitumens in such amount as to be worthy of consideration in this connection. This method is not recommended as superior to the method of Carius in ultimate research, but is recommended for the determination of sulphur in solid and semisolid bitumens for practical purposes.

May 1, 1899.

[A CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY,
UNIVERSITY OF MICHIGAN.]

**A NEW METHOD FOR THE DIRECT DETERMINATION
OF ALUMINA IN PRESENCE OF IRON, MAN-
GANESE, CALCIUM, AND MAGNESIUM.**

BY WILLIAM H. HESS AND E. D. CAMPBELL.

Received June 17, 1899.

THE method most commonly used for the determination of alumina in presence of iron, manganese, calcium, magnesium, and phosphoric acid, is the indirect method in which the iron, alumina, and phosphoric acid are obtained together as a combined precipitate with ammonia. The alumina is taken as the difference obtained by deducting the weight of phosphorus pentoxide and ferric oxide as determined in separate samples. While the determinations of phosphoric acid, as well as the volumetric estimation of iron are satisfactory, an error may be introduced by careless ignition of the mixed oxides, since ferric oxide may be more or less converted to magnetic oxide (Fe_3O_4), with loss of oxygen; while in the calculations all the iron is figured as ferric oxide. Any error arising from careless ignition, from failure to perfectly wash the precipitate, or from an imperfect separation of other substances present as calcium, zinc,

nickel, etc., goes to increase or decrease the percentage of alumina found.

Among the direct methods for determining alumina, the best known and most used are the alkali method and the thiosulphate method of Wöhler. Neither of these succeed satisfactorily when only traces of alumina are present with iron. Neither the potassium cyanide method nor the basic nitrate method of Beilstein and Luther seem to have become popular. These methods, as well as many others that have been worked out, either require special expensive platinum apparatus or much attention to detail to obtain the correct conditions. In short, the present direct methods for estimating alumina are laborious, and too uncertain in their accuracy to pay for the heavy labor entailed, and consequently have not as yet displaced the simple though somewhat uncertain indirect method.

A method for the direct determination of alumina in presence of other substances commonly occurring with it, which is accurate, simple and rapid, would seem to be of great practical value, especially to those chemists connected with the iron ore industry, with cement and other clay industries, as well as in general mineral analysis.

While engaged in trying to modify the old alkali process so as to make it more satisfactory, experiments were carried on with a view of finding some reagent which would quantitatively precipitate alumina without precipitating iron. Recourse was taken to the organic bases for a suitable reagent for this purpose.

The well-known ammonium base, phenylhydrazine, which has proved of such great value in establishing the chemistry of the sugars, was found to be the most satisfactory of the many organic bases tried for the precipitation of alumina. As a base it is somewhat weaker than ammonia. It precipitates aluminum from its solutions quantitatively as the hydroxide without a trace of the precipitate being redissolved in excess of the precipitant. Phenylhydrazine is, moreover, a strong reducing agent, quickly reducing iron from the ferric to the ferrous state, thus playing a double rôle of usefulness in the separation of iron from alumina.

METHOD OF ANALYSIS.

A convenient sample to be analyzed is weighed out and

obtained in solution preferably as the chloride in the usual way. To a convenient bulk of solution, 200 to 300 cc. heated to near the boiling-point, dilute ammonia is added slowly as long as the precipitate formed just redissolves with readiness. A neutral, saturated solution of ammonium bisulphate¹ is added, drop by drop, with stirring to this hot and nearly neutral solution, until it becomes colorless, showing the complete reduction of the iron. To the hot solution now smelling strongly of sulphur dioxide, one or two cc. of phenylhydrazine are added. If this amount of phenylhydrazine causes a permanent precipitate, then a few drops more of phenylhydrazine are added to insure complete precipitation of the alumina. If one to two cc. of phenylhydrazine do not produce a permanent precipitate, it is economical, after adding this amount of phenylhydrazine, to add dilute ammonia carefully, drop by drop, to a just perceptible permanent precipitate, and then complete the precipitation by adding a few drops more of phenylhydrazine. The precipitate, consisting of aluminum hydroxide and aluminum phosphate, is filtered out on an ordinary filter and washed with warm water containing a small amount of phenylhydrazine bisulphite. This washing solution is prepared as follows: To a few cubic centimeters of phenylhydrazine in a beaker, a saturated water solution of sulphur dioxide is added gradually until the precipitate of phenylhydrazine sulphite, which at first separates out in crystals, is redissolved to a yellow solution. If, after a few minutes, an odor of sulphur dioxide is perceptible, a few drops of phenylhydrazine are added to neutralize this excess of sulphurous acid. This concentrated solution of phenylhydrazine bisulphite, if well stopped, will keep indefinitely. Five to ten cc. of this to 100 cc. of water is an efficient strength of solution for washing the precipitate of alumina. The washing with this warm solution is continued until the washings give no test for iron with ammonium sulphide. A drop or two of phenylhydrazine is added to the filtrate with stirring to see if the precipitation has been complete. If chlorides of metals other than iron be present, the washing must be continued until the washings are free from chlorine. The presence

¹ (This solution of ammonium bisulphite is made by passing sulphur dioxide into a cooled solution of ammonia (1 : 1) until the solution becomes yellow. It serves the purpose here, not only of reducing the iron, but the excess of sulphurous acid unites with the phenylhydrazine added, to form a salt which acts as a most efficient agent for keeping the iron reduced and thus prevents its precipitation with the alumina.)

of chlorides of volatile bases will do no harm in the ignition of alumina.

The precipitate together with the filter is placed in a platinum crucible, dried and the filter charred at a low temperature. After the filter is completely burned, the ignition is continued at a bright red heat to constant weight. Care is taken to weigh quickly with the cover on the crucible, since both the phosphate and oxide of aluminum are very hygroscopic. A second ignition and weighing is always necessary. This precipitate of alumina carries all the phosphorus pentoxide so that the weight of alumina is found by subtracting the weight of phosphorus pentoxide found in a separate sample.

Chromium is quantitatively precipitated by phenylhydrazine, and may thus be separated from iron with great readiness. Neither calcium, magnesium, manganese, cobalt, or nickel is precipitated.

GRAVIMETRIC METHOD FOR IRON.

If a gravimetric estimation of the iron is desired, it has been found to be most expedient to add ammonium sulphide to the filtrate in case there is no other metal present that will be precipitated by this reagent. The sulphide of iron thus formed is filtered out, and without washing is redissolved in dilute hydrochloric acid. From this hydrochloric acid solution the iron is estimated in the usual way with ammonia after oxidation with nitric acid. It may under some circumstances be desirable to separate the iron and alumina by means of ammonia or as basic acetate, to get rid of other metals before attempting their specific separation by means of phenylhydrazine.

SEPARATION AND ESTIMATION OF PHOSPHORIC ACID.

Since the aluminum hydroxide precipitated with phenylhydrazine carries all the phosphorus pentoxide with it that is present in the solution, this method may be conveniently used for its separation. If the alumina present in the mineral is not sufficient to carry all the phosphoric acid as the normal phosphate, an excess of a known solution of aluminum chloride is added. The alumina is then separated by the above method. If only the phosphoric acid is desired, this precipitate may be dissolved in nitric acid and the phosphoric acid may be deter-

mined in the usual way. Or the precipitate may be ignited and weighed, thus giving the combined weight of alumina added, of alumina in the mineral and of phosphoric acid in the mineral.

RESULTS ON KNOWN MIXTURES.

Mixtures were made by Prof. Campbell's private assistant which were strictly unknown to the operator, and were subjected to the above method of analysis with results as recorded in the following table:

	Weight of iron taken. Gram.	Al ₂ O ₃ taken. Gram.	P ₂ O ₅ taken. Gram.	P ₂ O ₅ + Al ₂ O ₃ taken. Gram.	P ₂ O ₅ and Al ₂ O ₃ found. Gram.	Gain or loss. Gram.
(1)	0.7023	0.00664	0.00077	0.000741	0.000735	0.00006
(2)	0.2020	0.1343	0.00022	0.13452	0.1343	0.00022
(3)	0.059934	0.0105	0.00576	0.01581	0.0162	0.00039
(4)	0.3339	0.0966	0.01072	0.10732	0.1066	0.00072
(5)	0.6604	0.030	0.00577	0.03577	0.03570	0.00007
(6)	0.551	0.05152	0.01073	0.06225	0.06220	0.00005
(7)	0.527	0.0219	0.01073	0.03263	0.0330	0.00037
(8)	0.564	0.0644	0.00822	0.07262	0.0719	0.00072

A solution was prepared by dissolving one gram of calcium carbonate, 0.200 gram magnesium carbonate, 0.571 gram of ferric oxide, and one gram of manganous chloride, in hydrochloric acid. To this solution, 0.09016 gram aluminum oxide, and 0.05234 gram of phosphorus pentoxide was added. The combined weight of alumina and phosphorus pentoxide taken was therefore 0.1425 gram. The weight found was 0.1428 gram.

UNIVERSITY OF MICHIGAN,
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THE DETERMINATION OF ANTIMONY IN ORES.

BY THOMAS BROWN, JR.

Received May 9, 1899.

THE object of this paper is not to present new methods, but on the other hand the application of some very old ones which have been agreed upon by the buyers and sellers for determining antimony in ores, and which after trial have been proved to give more closely agreeing and satisfactory results than those formerly obtained by the many more widely used volumetric and gravimetric methods. In addition such observations and innovations in using these methods will here be mentioned as have been made by the writer in an experience of a year or so in analyzing the Mexican ores for the large exporters.

Only a limited number of commercial chemists both on this continent and in Europe are now engaged in doing this kind of work, because of the past wide variation in results frequently reported on the same sample, caused doubtless by the use of methods not so applicable to this class of ores, which is a matter of much importance considering the large shipments made from Mexico. The following list is of interest in showing the percentages of antimony reported on the same samples of Mexican ores by three prominent English commercial analysts before definite methods had been settled upon, and also the necessity for such a procedure. A, B, and C represent the results of these three chemists, B and C being of London, and D the percentage finally agreed upon in settling.

Sample No.	A.	B.	C.	D.
I	59.96	55.25	56.1	55.6
II	55.8	53.62	52.0	52.8
III	57.27	54.02	54.2	54.1
IV	58.13	54.5	54.8	54.6
V	60.78	59.23	63.1	60.0
VI	57.45	53.7	53.6	53.6
VII	53.5	54.4	53.9
VIII	59.8	53.2	54.9	53.5
IX	53.2	52.0	57.8	52.6
X	50.4	51.5	50.9
XI	52.4	53.7	53.0
XII	51.7	53.2	52.4
XIII	46.03	47.7	46.8

These ores are known to the trade as "clean ores," it being of rare occurrence to find impurities in the grades shipped other than silica, iron, and lime which obviously would not interfere with the schemes of analysis used. The metals of the fifth and sixth groups sometimes found accompanying antimony in ores, such as lead, mercury, copper, tin, and arsenic, when found in quantities larger than traces should be separated from the antimony when it is to be determined by the method used for sulphides, and also tin and arsenic when the antimony is to be determined by the oxide method. Shipments of ore from an unknown locality should consequently be put through a series of preliminary tests, and it is always advisable to test every sample for the most common impurities such as lead and arsenic; qualitatively for the purpose of modifying the sulphide method

and quantitatively if found in appreciable quantities, because of having to be taken into consideration in estimating the market value of the ore.

Lead is determined both qualitatively and quantitatively as the orange-yellow chromate (PbCrO_4). For the qualitative test the finely ground ore is boiled with concentrated nitric acid for several minutes, and, if a sulphide, until the sulphide of antimony is entirely converted into the insoluble white oxide, then cooled and diluted. Ammonia is added in excess, then acetic acid in excess, and the whole heated for several minutes in order to bring the lead salts thoroughly into solution. The insoluble matter is now filtered off, and the filtrate treated with an excess of potassium bichromate which precipitates the lead as chromate from this ammonium acetate and acetic acid solution. The lead can also advantageously be determined quantitatively in this form from the sulphide precipitate remaining on the filter after separating the antimony from the metals of the fifth group as will be explained later in the scheme of analysis.

For arsenic a combination of the Canby and Mohr methods is used. One gram of the finely powdered ore is mixed in a porcelain crucible with eight to ten parts of a mixture of equal parts of sodium carbonate and niter, gradually brought to fusion over a burner or in a muffle and kept so for five minutes or more. The fused mass is allowed to cool, disintegrated in hot water and the insoluble matter filtered off. The filtrate is now acidified with nitric acid and the carbonic and nitrous acid gases boiled off. An excess of an emulsion of zinc oxide, so apparent in the bottom of the beaker, is added, and should an unusually heavy precipitate of gelatinous silica and alumina be produced, a second filtration is necessary, also an extra addition of zinc oxide to the filtrate before the precipitation of the arsenic. This is precipitated as the reddish brown silver arsenate (Ag_3AsO_4) by the addition of silver nitrate in slight excess accompanied by vigorous stirring.

The precipitate mixed with zinc oxide is filtered, washed with cold water until the washings show no silver reaction, and dissolved off the filter with hot dilute nitric acid, catching the solution and washings in a beaker free from chlorine. When cold this is titrated for silver with an empirical solution of potassium

or ammonium thiocyanate using one cc. of a saturated solution of ferric sulphate as indicator, and titrating to the same pale amber-yellow color as was obtained in standardizing the solution against pure silver. For the standard silver solution one gram of the pure metal is dissolved in nitric acid, boiled to expel red fumes and diluted to 100 cc. For the standard thiocyanate solution nine and three-tenths grams of potassium thiocyanate or seven and six-tenths grams of ammonium thiocyanate are dissolved and diluted to one liter; then 1 cc. = 0.010 gram silver, and 108 silver = 25 arsenic. This same treatment somewhat modified is used in testing the ore qualitatively for arsenic. After fusion, the addition of acid, boiling and the addition of zinc oxide in excess, the whole is filtered and the neutral filtrate tested for arsenic as before.

The antimony ores of Mexico most common to the trade are those of stibnite (Sb_2S_3); cervantite (Sb_2O_3) produced by the oxidation of the former; oxysulphides, mixtures of these two with a preponderance of the former, and senarmontite (Sb_2O_3) which is, however, of much rarer occurrence. The composition of the oxide may be inferred from its behavior when boiled with concentrated hydrochloric acid with the subsequent addition near the end of the treatment of a few drops of nitric acid. Cervantite treated thus is but sparingly soluble, while senarmontite is almost if not completely so. Stibnite is also completely soluble; if, however, the ore be an oxysulphide as is frequently the case, insoluble oxide of antimony is found in the siliceous residue which is afterwards determined by fusion.

The following analysis of an ore from the state of Oaxaca illustrates this statement in regard to the solubility of these oxide ores: Moisture, 0.3; silica, 8.5; iron oxide and alumina, 1.6; iron pyrites (FeS_2), 0.9; lime and magnesia, traces; cervantite (Sb_2O_3), 3.8; senarmontite (Sb_2O_3), 84.7; total, 99.8. The results of a complete analysis being calculated to their probable composition, left a difference of 88.7 per cent., to be filled by the 70.8 per cent. soluble and the three per cent. insoluble antimony found, and which were calculated to the composition of senarmontite and cervantite as they were shown to be by their solubility.

Upon the behavior of these ores when treated with concentra-

ted hydrochloric acid plus a few drops of acid and boiling, is based their division into the following three classes for applying the schemes of analysis: 1. The soluble ores—stibnite (and senarmontite); 2. The practically insoluble ores—cervantite; 3. The partially soluble ores—the oxysulphides, stibnite mixed with cervantite.

1. *The Soluble Ores.*—For the “soluble ores” one gram, which has been finely pulverized in an agate mortar, is treated in a No. 3 beaker with twenty-five cc. concentrated hydrochloric acid, covered and boiled on a plate or over a flame until apparently decomposed and the solution is not more than fifteen cc. in bulk. About two grams of tartaric acid are added, and as soon as that is dissolved about four to six drops of concentrated nitric acid, and the whole is boiled for a minute or so more. This last addition causes a violent reaction and a more complete decomposition. The beaker is now removed from the source of heat, the cover and sides washed down, the insoluble residue filtered out and the filtrate and washings diluted in bulk to about 250 cc. A steady stream of hydrogen sulphide gas is now run through the solution for about an hour until it is thoroughly saturated and the antimony thus precipitated as the amorphous orange-colored sulphide (Sb_2S_3).

To insure a complete precipitation this is gently warmed in order to convert any basic chloride into sulphide and then allowed to stand an hour or so in the cold before filtering. The filtrate will then be perfectly clear and not deposit additional antimony upon standing or upon further treatment with hydrogen sulphide gas. Should lead or other impurities of the fifth group have been found by the preliminary qualitative tests, after filtering and washing the precipitate with cold water it is washed back into the beaker in which it was precipitated and treated with ammonium sulphide in such excess that with the aid of heat the antimony precipitate completely dissolves. The solution is then run back through the same filter, caught in a clean beaker and the filter thoroughly washed with hot water. The solution and washings are acidified in slight excess with hydrochloric acid, reprecipitating the antimony sulphide, diluted to about the same bulk as before (250 cc.), allowed to stand a few minutes to settle and then filtered. In the black sulphide

residue remaining on the filter representing the impurities of the fifth group, the lead may now be determined by placing the filter containing this precipitate into a beaker, treating with nitric acid and boiling, adding ammonia in excess, then acetic acid in excess, filtering, reprecipitating the lead as chromate and weighing it thus on a Gooch crucible or balanced filter-papers.

The antimony sulphide precipitate, whether precipitated but once or reprecipitated for purification, is now washed well upon a large, plaited, balanced filter with cold water and dried in an air-bath at 110° C. for two hours or more to constant weight. After removal and as soon as cold the weight of the dried precipitate is taken which consists of antimonous sulphide (Sb_2S_3) mixed with a small amount of free sulphur.

The following procedure has been found both rapid and accurate for weighing this precipitate. A German corrugated filter, 15 cm. in diameter, is used. Two are selected which lay beside one another in the same pack and which from long impact contain practically the same amount of moisture. They are balanced by cutting down the heavier one. Upon the unaltered one the precipitate is filtered, the other accompanying it in the drying oven and as a counterpoise in weighing. When the weight of the precipitate has thus been determined it is carefully scraped from the paper and powdered and mixed well by grinding in a small glass mortar. A certain amount of this (fifteen tenths gram) is weighed off into a platinum boat, this introduced into a glass combustion tube and the free sulphur driven off in a stream of carbon dioxide. From the weight of the resulting black anhydrous antimonous sulphide so obtained on a weighed amount of the dried precipitate, its total weight thus treated can easily be calculated, and it is then simply a matter of calculation to determine the total amount of antimony present. $\text{Sb}_2\text{S}_3 \times 0.7177 = \text{Sb}$.

The combustion requires in all from twelve to fifteen minutes, and if carefully conducted with the following precaution, very little loss if any at all occurs. Arsenic if present would be volatilized. (a) A steady stream of gas should be passing through the tube when the flame is applied underneath the boat, and should continue so with as little variation as possible until the end of the operation. Should this not be the case, a flame

would at first play over the surface of the contents of the boat causing oxidation apparent to the eye when removed from the tube by a whitening of the surface and consequently a loss in weight. (b) The heating of the boat in the tube should be accomplished gradually. At first a gentle heat is applied until all the sulphur has apparently been driven off, and increased towards the end of the operation. (c) The tube should be cleaned of sublimed sulphur by heating before each and every determination. After weighing the boat and contents it is well to treat again for additional loss in weight, which is rarely found if the operation has been conducted as described.

2. *The Practically Insoluble Ores.*—The important point here is the decomposition of the ore which is accomplished by fusion. One gram of the finely powdered ore is mixed with eight to ten parts of a flux composed of equal parts of flowers of sulphur and sodium carbonate, introduced into a porcelain crucible (capacity forty cc.), and in addition the mixture is covered with a thin layer of the flux. The covered crucible is introduced into the opening of a muffle that is of a bright red heat and is cautiously heated to fusion for about ten minutes. The heat applied at first should be of such an intensity that sulphur flames are barely seen escaping around the edge of the lid; after they cease it is somewhat increased by pushing the crucible a few inches farther back in the muffle. At no time should the crucible become heated to more than perceptible incandescence on the side facing the source of heat, and during the operation it should be occasionally turned with a pair of tongs to insure an even heating and consequently a complete decomposition. The color of the melt when cold should be green, not yellow, and likewise the solution of the same due to the sulphide of iron present. A suggestion of a yellow color particularly in the solution indicates an incomplete decomposition of the ore, and but a partial change of the antimony into the soluble sodium sulphantimonate which consequently necessitates a repetition of the fusion.

A successful fusion owing to the ready volatility of antimony at a comparatively low degree of heat is rather a delicate thing and difficult to accomplish, requiring constant care and judgment only gained by experience. With the statement that it is possible to thoroughly decompose such an ore by fusing over a

candle flame, the writer is compelled to differ, having frequently found that a fusion made at a seemingly alarming degree of heat gave when dissolved a yellow solution in which the antimony when determined was found to be lower than that of a duplicate sample which had been treated to a higher degree of heat. It is, therefore, better to treat in excess than not to fuse enough; for should there be a slight loss by volatilization, this would in a measure be counterbalanced by the small amount of impurities, such as silica, obtained from the action of the flux on the crucible and on the silica of the ore, and consequently thrown down by the acid and weighed with the antimony sulphide precipitate. The degree of heat used, however, should scarcely effect the glaze of the crucible. When the fusion has thus been satisfactorily accomplished and when cool, it is dissolved in hot water, which takes but a few minutes, the suspended precipitate of iron sulphide and sulphides of the metals of the fourth group, if present, filtered off, and the antimony precipitated by adding a slight excess of hydrochloric acid to the filtrate. After stirring and allowing to stand a few minutes to settle the precipitated antimonious sulphide (Sb_2S_3), mixed with more or less free sulphur, is filtered off upon a balanced filter and so determined as before, being ultimately weighed when removed from the combustion tube as antimonious sulphide (Sb_2S_3).

3. *The Partially Soluble Ores.*—These ores require a double treatment, that is they are first treated as for soluble ores and the antimony determined in the acid solution, and the residue, remaining on the filter which contains the undissolved oxide, is subjected to a fusion as for oxide ores. This filter-paper is placed in the bottom of a porcelain crucible and covered well with flux so that some comes in direct contact with its contents. It is then fused as directed. In dissolving, pieces of charred paper may possibly be found, which are, however, filtered out together with the insoluble matter. The amount of antimony so present is determined as before.

Most Mexican so-called sulphide ores exported are really oxy-sulphides being mixtures of sulphide with a small amount of oxide which has not been separated in the sorting; these ores consequently require this double treatment. The following is a list of results obtained in using these methods upon the pre-

viously mentioned varieties of Mexican ores, and gives in the case of oxysulphides the soluble and insoluble antimony found. In the last column will also be found the results by the fire assay, which is extensively used on oxide ores for prospecting work, and also for large shipments when the "wet assay" is to be made later at their destination. It is figured by the dealers that the wet assay of a sixty per cent. ore will go six per cent. higher than the dry or fire assay. That there are exceptions to this will be seen in Nos. 5, 8, and 12 of the table. No. 5 is the senarmontite ore, the complete analysis of which has already been given, while Nos. 8 and 12 are quite insoluble under the acid treatment leading to the supposition that they are cervantite ores of the composition Sb_2O_3 . It has also been observed that certain grades of oxide ores give higher results by fire assay than other grades, which is considered due to their ultimate composition of which very little is so far known. The widely different and extremely low results obtained by fire assay upon sulphide ores makes them no criterion upon which to judge of the actual antimony present, and so for this class of ores it is falling into disuse.

No.	Class of ore.	Soluble Sb.	Insoluble Sb.	Total Sb.	Fire assay.
1.	Sulphide	67.4	..	67.4
2.	"	28.5	..	28.5
3.	Oxysulphide ...	61.6	5.1	66.7	48.0
4.	" ...	63.3	6.7	70.0	45.0
5.	Oxide	70.7	3.1	73.8	72.8
6.	"	71.7	65.0
7.	"	66.1	59.0
8.	"	63.9	61.8
9.	"	55.8	49.0
10.	"	49.0	43.0
11.	"	48.3	43.0
12.	"	46.4	44.4

The fire assay referred to consists of the reduction of the contents of the ore to the metallic state by fusion with potassium cyanide and while it is known that it is possible to obtain higher results by the use of other mixed fluxes together with a treatment for a longer time at a lower heat, this cyanide reduction remains the accepted method in trade. It is performed as follows : Five grams of the powdered ore is mixed with twelve

parts of potassium cyanide, placed in a ten gram clay crucible and covered with salt. The fusion is made in a muffle at a bright red heat, allowing it to remain there thirteen minutes. When removed it is thoroughly shaken to collect the globules into one metallic button and allowed to cool. The crucible is broken and the resulting button carefully broken from the slag and weighed.

In conclusion the writer desires to express his obligation both to Mr. M. Elsasser and to Mr. Ferdinand McCann for their kind assistance in furnishing him with suggestions, data, etc., without which this paper would not have been written.

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ELECTROLYTIC DETERMINATION OF ZINC IN THE PRESENCE OF MANGANESE.

BY EMIL J. RIEDERER.

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IN determining zinc quantitatively by means of the electric current, it is essential to have the zinc in the form of sulphate and there should be neither nitrates nor chlorides present.

It was found best to use a platinum dish, on which silver had been deposited, for a cathode. In the first experiments, I tried copper deposits on platinum, but discarded this owing to the fact that copper is too easily oxidized, and consequently causes variation in weight. During the deposition of zinc it is found best to stir the solution (using a mechanical stirrer) continually, so as to obtain an even and uniform deposit; and to keep the temperature under 26° Celsius.

The current used for the deposition of zinc was four volts, giving a current of three and five-tenths volts and 0.20 to 0.26 amperes for 100 sq. cm. of cathode area. The current may vary from 0.20 to 0.26 amperes and the temperature from 15° to 26° Celsius.

Different proportions of zinc and manganese were tried so as to determine the action of the manganese, but in no case could any traces of manganese be found in the zinc which was deposited on the cathode.

The following reagents were used for the electrolysis:

a. A solution of lactic acid ($\text{CH}_3\text{CHOH.COOH}$, each

cubic centimeter of which contained 0.937 gram of lactic acid.

b. A solution of ammonium lactate ($\text{CH}_3\text{CHOH.COONH}_4$) each cubic centimeter of which contained 0.50 gram of ammonium lactate.

c. Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, crystalline.

The volume of the solution in all cases was 230 cc.; the cathode surface 150 sq. cm., and the anode one and one-half cm. distant from the cathode.

The zinc and manganese salts used were the sulphates $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$.

ANALYSIS No. 1.

Zinc sulphate	0.5074 gram
Manganese sulphate	0.1634 "
Ammonium lactate.....	5.0000 "
Lactic acid.....	0.7500 "
Ammonium sulphate	2.0000 "
Ampere, varying from	0.24-0.26 N.D. ₁₀₀
Voltage, " "	3.7-3.9
Temperature varying from.....	20°-25° C
Percentage of zinc found.....	22.786
" " " theory	22.78
Time required to deposit zinc completely....	4 hours, 10 minutes

No traces of manganese were found in the zinc.

ANALYSIS No. 2.

Zinc sulphate.....	0.5000 gram
Manganese sulphate	0.4466 "
Ammonium lactate	5.0000 "
Lactic acid	0.7500 "
Ammonium sulphate ...	2.0000 "
Ampere varying from	0.2-0.22 N.D. ₁₀₀
Voltage " "	3.5-3.8
Temperature varying from	15°-22° C.
Percentage of zinc found	22.82
" " " theory	22.78
Time required to deposit zinc completely....	4 hours, 10 minutes.

ANALYSIS No. 3.

Zinc sulphate	0.5000 gram
Manganese sulphate.....	2.0000 "
Ammonium lactate.....	5.0000 "
Lactic acid	0.3800 "
Ammonium sulphate	2.0000 "
Ampere varying from	0.2-0.23 N.D. ₁₀₀
Voltage " "	3.0-3.6
Temperature varying from.....	18°-24° Celsius
Percentage of zinc found	22.72
" " " theory	22.78
Time required to deposit zinc completely ...	5½ hours

In all I have made about sixteen separations of zinc from manganese in the manner described, but in only two cases did the electrolysis require more than five and one-half hours, or did the result vary more than 0.10 per cent. from the theoretical value. Constant stirring was found to give a more rapid and uniform silver-like deposit of zinc.

In several cases manganese hydroxide was found on the anode, in small amounts during the electrolysis, but in no case could any traces of manganese be found in the deposited zinc.

During every electrolysis containing manganese, it was noticed that the solution turned from colorless to amethystine, the more manganese present the darker the color. On allowing this solution to stand for a short while, after having removed it from the platinum dish, and disconnected the current, it was noticed that the solution again became colorless.

It was found that the best results were obtained between the temperatures of 15° and 28°C. If below 15° C. the electrolysis requires longer, if above 28° C. the zinc may deposit in such a manner (either large crystals or even spongy) as might cause loss in washing. The amount of zinc deposited in each electrolysis should not be more than 0.1700 gram of pure zinc.

After the electrolysis is completed the solution is poured off, the zinc deposit washed with distilled water, alcohol, and finally with pure ether to remove alcohol; then place a in the hot water oven to dry perfectly, then placed in a desiccator until ready for weighing. This washing and drying should not require more than five minutes.

When an electrolysis is started the current should be regulated to 0.25 ampere N.D.₁₀₀, and if the temperature is between 15° and 28° C. it will be found that during the entire process the current will vary but slightly.

If the current is increased to more than 0.30 ampere N.D.₁₀₀ (normal density of current for 100 sq. cm. of cathode area) it is found that the zinc will not be deposited evenly, and more manganese hydroxide will be found at the anode; also that the zinc being deposited so quickly, and in larger crystals, will mechanically enclose some manganese or solution. If the current is less than 0.20 ampere N.D.₁₀₀ the time required for complete deposition will be longer.

The solution from which zinc is to be deposited should always be neutral or slightly acid.

These experiments were made during 1897-1898 in the laboratory of the Koenigliches Polytechnikum in Munich, Germany.

[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 40.]

THE INFLUENCE OF SUBSTITUENTS ON THE ELECTRICAL CONDUCTIVITY OF BENZOIC ACID.¹

BY ALFRED TINGLE.

Received July 24, 1899.

INTRODUCTORY.

VICTOR MEYER and his pupils have shown that in a substituted aromatic acid, the rate of esterification is affected by the nature and position of the substituting atoms or groups. Kellas² proved that for monochlor-, monobrom-, and moniodobenzoic acids, the rate of esterification varies with the molecular weight of the acid, or in other words, with the atomic weight of the substituting halogen. Thus, graphically represented, when the molecular weight of the acid is taken as the abscissa, and the percentage of ester formed in a given time, as the ordinate, a straight line is obtained.

No attempt appears to have been made, even in view of this work, to examine the effect of the position and nature of a substituent on the electrical conductivity of the aromatic acids. The conductivities of substituted benzoic acids have been examined by many investigators, but usually with the view of determining their affinity coefficients, and with little regard for the nature of the substituting group.

The conductivities of salts of organic acids have also been investigated, notably by Ostwald, but never, as it would appear, with the view of finding any relation between the conductivities in question and the atomic weights of the metals forming these salts.

The present investigation was undertaken with the object of examining into the changes introduced in the conductivity of benzoic acid, by the substitution of various metals for the

¹ From author's thesis for the Ph.D. degree.

² Kellas: Inaugural Dissertation, Heidelberg, 1897.

hydrogen of the carboxyl group, and of halogens for the hydrogen of the benzene nucleus.

It was hoped that these substituting elements might be found to have an influence traceable to their position in the periodic table. It was further thought possible that some definite relationship might be disclosed between the conductivities of position-isomers.

With these objects in view, the elements substituting carboxylic hydrogen were entirely selected from Group I of the periodic table, while those entering the nucleus in the two chosen positions ortho and para were from Group VII.

We are thus in a position to see:

1. What is the effect on its electrical conductivity of introducing an alkali metal into the carboxyl group of benzoic acid, and how this effect varies with the atomic weight of the metal.

2. What effect is produced on its electrical conductivity when, in a salt so formed, a hydrogen atom is replaced in the ortho, or in the para position, by one of the heavier halogen atoms.

The work described in the pages which follow is of a purely preliminary nature, and no claim to extreme accuracy is made.

Several factors militate against any such claim, notably the small quantities of substance available in some cases, with a consequent absence of certainty that purification was thorough. Another objection, which may plausibly be made, is that the conductivity of the water employed was comparatively high, so rendering the correction to be applied somewhat uncertain.

Nevertheless it is believed that the approach to accuracy is sufficiently near to show certain points which merit further investigation. Some idea as to this degree of accuracy may be gained by noting the extent of agreement, where, for any reason, determinations of conductivity have been made from separately prepared samples of the same compound.

Perhaps it should be noted that many of the salts studied in this research have not hitherto been elsewhere described.

PRACTICAL.

Preparation of p-Brombenzoic Acid.—Commercial toluene was brominated in the usual manner. The resulting product was

repeatedly fractionated, those portions passing over between 130° and 190° being collected. The bromtoluene so obtained was heated with an excess of nitric acid (one part concentrated acid to three parts water) till oxidation to the corresponding acid was complete. The crystals which separated, on cooling, from a large volume of the acid liquid were found to have the melting-point 248° (melting-point of *p*-brombenzoic acid, 251°). They were purified by repeated extraction with hot water, and were finally recrystallized from alcohol till they possessed the constant melting-point of 251° - 252° .

*Preparation of o-Brombenzoic Acid.*¹—This acid was obtained from *o*-amidobenzoic acid by the Sandmeyer reaction. The crude product was repeatedly crystallized from water, converted into its barium salt, reobtained by treating this with hydrochloric acid, and finally crystallized from dilute alcohol until it possessed a constant melting-point.

Preparation of p-Iodobenzoic Acid.—*p*-Iodobenzoic acid was obtained by the oxidation of *p*-iodotoluene. Chromium trioxide and glacial acetic acid were at first used for this purpose; it was subsequently found that boiling with dilute nitric acid was a much preferable means of procedure. By the latter method the oxidation seems to be quite as rapid and as readily controlled. It is also much easier to obtain the product in a pure form. The products obtained by the above two methods were mixed together and carefully sublimed. The acid was then further purified by crystallization from slightly dilute alcohol; it then had the melting-point 267° - 268° .

Preparation of o-Iodobenzoic Acid.—This was obtained by two processes. A part of the acid employed was made by oxidizing *o*-iodotoluene with boiling dilute nitric acid. This seems to be the best method, even the crude product being very nearly pure. It was necessary, however, to obtain the greater part of the acid used in these experiments from *o*-amidobenzoic acid by the Griess reaction. The acid obtained in this way was purified by repeated crystallization from hot water, till it possessed the correct melting-point. It was mixed with the portion of acid obtained by oxidizing *o*-iodotoluene, and the whole was then twice recrystallized.

¹ For the preparation of this and of the similarly obtained *o*-iodobenzoic acid, I am indebted to my fellow-student, Mr. T. M. Taylor.

Purification of Benzoic Acid.—"Chemically pure" benzoic acid was dissolved in hot water, the solution filtered, and allowed to crystallize. The product was again crystallized from water, when its melting-point remained unaltered and correct.

Preparation of Pure Water.—The method adopted was a slight modification of that suggested by H. C. Jones and Mackay.¹ The only change made, at first, was that of substituting a well-steamed hard glass condenser for the block-tin condenser employed by these workers. The water so obtained was, of course, inferior in purity to that obtained by them, but was considered to be sufficiently pure in view of certain other sources of error. It was of fairly uniform quality, the average conductivity being 4.4×10^{-6} mercury units. In every case a correction has been applied, based upon a determination of the particular sample of water employed. It was later found that much time could be saved by refilling the washing retort, after each occasion on which the apparatus was cleaned, with an alkaline solution made from previously purified water. In this way it was possible to dispense with the use of potassium permanganate in the washing retort without the least danger of ammonia passing over, even in the first portions.

Method of Operation.—These conductivities were determined, by the method of Kohlrausch, at a temperature of 25°. The resistance capacity of the electrode vessel was found by using a solution of pure potassium chloride.

The bridge wire was one meter in length, and was not calibrated. In making up the solutions to be determined, a calculated quantity of the salt, dried at 120°–130°, was accurately weighed out, dissolved in water, and the solution brought up to the proper volume. Except where otherwise stated, the solution so obtained was $\frac{1}{4}$, the solution $\frac{1}{128}$ being generally prepared by diluting the stronger solution in the electrode vessel.

SALTS OF *p*-IODOBENZOIC ACID.

The method by which these salts were prepared is typical of that employed with all except the benzoates. The dry alkaline carbonates were accurately weighed and dissolved in water. To these solutions a calculated quantity of *p*-iodobenzoic acid was

¹ *Am. Chem. J.*, 19, 90.

added. The quantity of acid employed was about five-tenths milligram more than was necessary exactly to neutralize the alkali; it was considered impossible on account of adherent moisture, etc., to weigh out exact equivalents of acid and carbonate, but more easy to afterwards remove this slight excess of acid than a possibly unforeseen trace of alkali. The mixture so obtained was warmed on the water-bath till no further reaction could be observed to take place. It was then cooled and filtered (the acid being almost insoluble in cold water). The clear solution so obtained was evaporated to dryness on the water-bath, and the residue then crystallized from its most convenient solvent. The salt was next air dried, and finally dried at 120° – 130° as mentioned above.

Sodium p-Iodobenzoate.—This salt crystallized from water in needles.

Conductivity determination:

v	μ
64	66.04
128	67.39

Potassium p-Iodobenzoate.—The salt employed was crystallized from alcohol, and the crystals very thoroughly washed with ether.

Conductivity determination:

v	μ
64	74.66
128	77.05

Rubidium p-Iodobenzoate.—This salt crystallized in beautiful plates and needles from a mixture of alcohol and ether.¹

Conductivity determination:

v	μ
64	93.53
128	97.19

Cesium p-Iodobenzoate.—Crystallized from alcohol and ether, in needles.

¹ A mixture of alcohol and ether is not commonly employed, it is believed, in the crystallization of the alkali salts of organic acids. In the course of this work it has been frequently used with the best results, giving good, and very pure crystals. By the use of this solvent the waste incidental to recrystallizations was reduced to a minimum, while it was eminently calculated to remove any trace of acid. The method of handling the medium is to dissolve the salt in a little hot alcohol, allow this to cool somewhat, and add about five times its volume of ether.

Conductivity determination :

v	μ
64	88.18
128	90.48

SALTS OF *p*-BROMBENZOIC ACID.

The general method employed in preparing these salts was identical with that given under the salts of *p*-iodobenzoic acid.

Sodium p-Brombenzoate.—This salt did not readily crystallize from water. It was purified by the use of alcohol. In this medium it dissolved with some difficulty, separating when cool as a gelatinous precipitate, which dried to a somewhat horn-like mass.

Conductivity determination :

v	μ
64	65.14
128	67.10

Potassium p-Brombenzoate.—Crystallized from alcohol, in large plates somewhat resembling mica in general appearance. The crystals were washed first with a little alcohol, and then with much ether. In this case the two solutions employed were prepared independently, and from samples of the salt made at different times.

Conductivity determination :

v	μ
64	86.74
128	87.58

Rubidium p-Brombenzoate.—Crystallized from a mixture of ether and alcohol, in needles.

Conductivity determination :

v	μ
64	86.21
128	88.93

Cesium p-Brombenzoate.—Crystallized in needles, from a mixture of ether and alcohol.

Conductivity determination :

v	μ
64	83.71
128	88.03

SALTS OF *o*-IODOBENZOIC ACID.

The method applied to the preparation of the foregoing salts was also used here. The greater solubility of the ortho acid, however, made it necessary to use a small quantity of water in the first stages of these preparations.

Sodium o-Iodobenzoate.—Crystallized from alcohol-ether mixture.

Conductivity determination:

v	μ
64	64.21
128	67.35

Potassium o-Iodobenzoate.—Crystallized from alcohol-ether mixture.

Conductivity determination:

v	μ
64	78.94
128	83.36

SALTS OF *o*-BROMBENZOIC ACID.

The remarks on the preparation of *o*-iodobenzoates apply equally to these salts.

Sodium o-Brombenzoate.—Crystallized in magnificent feathery needles from a mixture of ether and alcohol. The two solutions ($v = 64$ and $v = 128$) employed were from different samples of the salt, and were made independently of one another.

Conductivity determination:

v	μ
64	66.11
128	68.02

Potassium o-Brombenzoate.—The purification of this salt offered some slight difficulty on account of its great solubility and the small quantity available for the work. It refused to crystallize from alcohol, with which it formed a somewhat oily solution. On the addition of ether to this, the ether quickly separated as a distinct layer, and failed to induce crystallization. The whole was therefore evaporated to dryness, and the dry salt so obtained quickly washed on the filter with a mixture of ether and a little alcohol.

Conductivity determination:

v	μ
64	86.92
128	90.92

SALTS OF BENZOIC ACID.

In preparing the benzoates in pure condition, the comparatively great solubility of benzoic acid offered a difficulty. This was, it is believed, overcome by prolonged gentle heating of the aqueous solutions on the water-bath, and the use of considerable volumes of alcohol in the later crystallizations.

Lithium Benzoate.—In this case advantage was taken of the comparative insolubility of lithium carbonate: this was weighed out in slightly greater quantity than that calculated for the previously weighed benzoic acid. The two were mixed in the presence of alcohol and warmed. On the reaction ceasing, the excess of lithium carbonate was filtered out, the solution evaporated to dryness and the residue dissolved in a little water. The solution was again filtered, and again evaporated to dryness. The salt was finally crystallized from a mixture of alcohol and ether.

Conductivity determination:

v	μ
64	57.30
128	59.67

Sodium Benzoate.—This salt did not crystallize at all well from water, but merely dried out on the sides of the beaker. It showed little tendency to dissolve in alcohol, and from this medium it was deposited in gelatinous form. The attempt at crystallization was therefore abandoned; the salt solution was evaporated to dryness, the solid mass repeatedly extracted with hot alcohol, and finally washed on the filter by the same liquid. From the foregoing it is evident that the purity of this sample of the salt must remain doubtful.

Conductivity determination:

v	μ
64	67.93
128	70.66

Potassium Benzoate.—This salt was crystallized from alcohol, in which it is very soluble, and was subsequently washed with ether.

Conductivity determination:

ν	μ
64	88.05
128	92.02

Rubidium Benzoate.—The salt is readily soluble in hot, but rather insoluble in cold, water, a property which rendered it all the more difficult to remove benzoic acid; in this case, therefore, the steaming of the salt on the water-bath was prolonged. It was ultimately crystallized from a mixture of ether and alcohol. From this medium it deposited in beautiful plates, but from water it appeared in the form of needles. Two preparations were made and their conductivities determined separately.

Conductivity determination:

ν	μ
64	92.04 (1st preparation)
64	91.48 (2d ")
128	94.33 (3d ")

Cesium Benzoate.—This salt appears to be more soluble in cold water than the foregoing. It was crystallized from alcohol and ether. The two solutions employed were made independently, from different samples of the salt.

Conductivity determination:

ν	μ
64	91.85
128	94.66

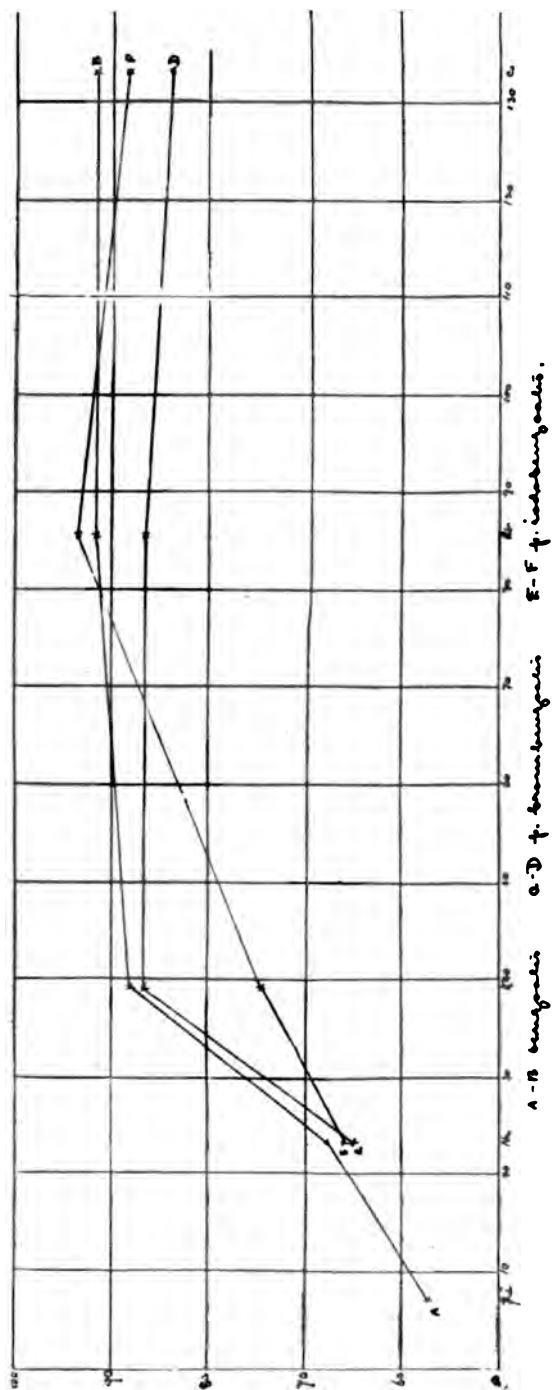
An attempt was made to determine the conductivity of lithium *p*-brombenzoate. The pure salt was obtained in solid form with difficulty, as it is very soluble in alcohol and appears to be somewhat soluble even in ether alone. On being placed between filter-paper and left over night, the crystals deliquesced completely. No further preparation of the salt was made. Lithium *o*-iodobenzoate was also prepared. It was obtained as a gummy mass, which, on long standing, became permeated with stellate groups of needles. On the addition of ether it immediately re-assumed its original gummy form, and the attempt to purify it was abandoned.

CONCLUSION.

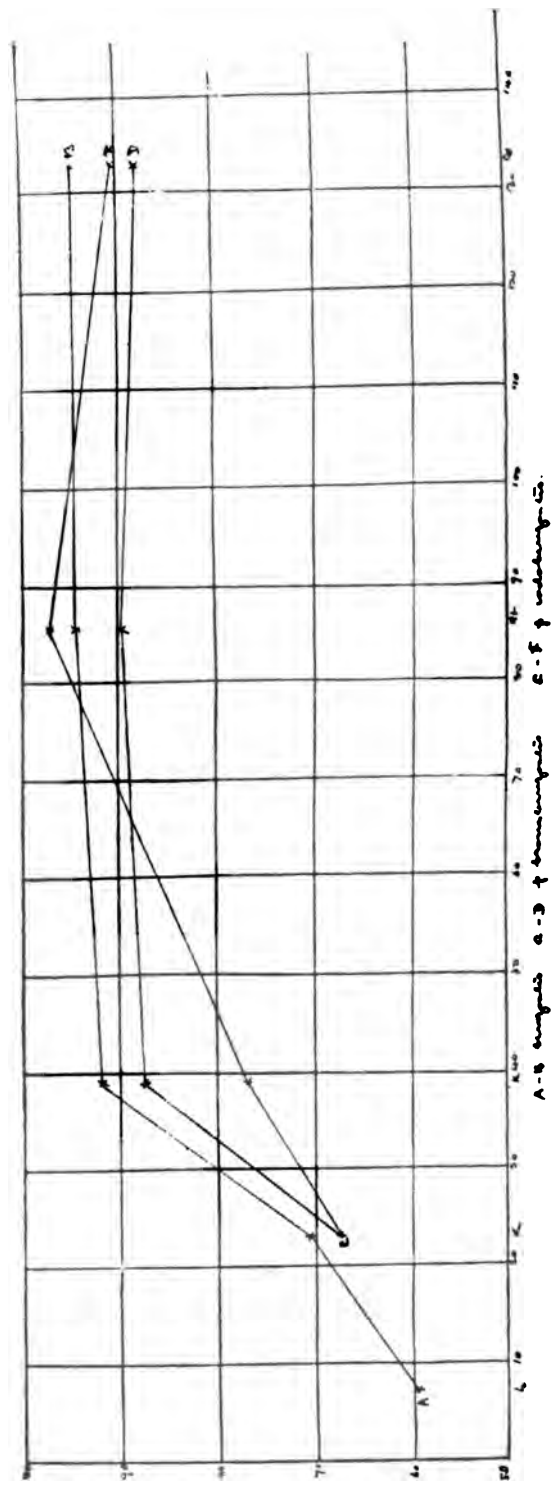
Ostwald¹ has experimentally shown, in a large number of cases, that where two metals form salts with the same acids, the

¹ *Ztschr. phys. Chem.*, 1, 74 and subsequent papers.

I v. 69.



11 $\sigma = 1.56$.



difference in conductivity of the same salts of the two metals is constant, and independent of the nature of the acids. He has also pointed out that this phenomenon is directly deducible from Kohlrausch's law of conductivity. A glance at the appended table of conductivities ($\nu = 64$), obtained in this research, will show that the variations from this rule are very marked in some cases, and are far in excess of what is believed to be the experimental error.

A graphic representation of the same table is given on Plate I, while Plate II shows the results when $\nu = 128$. The ordinates represent μ , and the abscissae the atomic weight of the metal. According to the law previously referred to, the curves, whatever their form, should be parallel, or at least approximately so, a condition which these do not fulfil.

In view of these variations, it seems necessary to refrain, for the present, from any attempt to draw theoretical conclusions from the results obtained. They are not final, but show that this series of salts requires further investigation. Perhaps, however, it may be allowable to point out that the departure from theory is much greater in the case of the potassium and sodium iodobenzoates than in those salts which the same metals form with acids of smaller molecular weight.

TABLE OF CONDUCTIVITIES.

($\nu = 64$.)

Salts of <i>p</i> -iodobenzoic acid.			Salts of <i>p</i> -bromobenzoic acid.		
Metal.	μ .	Difference.	Metal.	μ .	Difference.
Cs.....	88.18		Cs.....	83.71	
		5.35			2.50
Rb.....	93.53		Rb.....	86.21	
		18.87			0.53
K.....	74.66		K.....	86.74	
		8.6			21.60
Na.....	66.04		Na.....	65.14	
Salts of benzoic acid.			Salts of <i>o</i> -iodobenzoic acid.		
Metal.	μ .	Difference.	Metal.	μ .	Difference.
Cs.....	91.85		K.....	78.94	
		0.99			14.73
Rb.....	91.76		Na.....	64.21	
		3.71			
K.....	88.05		Salts of <i>o</i> -bromobenzoic acid.		
		20.12	Metal.	μ .	Difference.
Na.....	67.93		K.....	86.92	
		10.63			20.81
Li.....	57.30		Na.....	66.11	

NEW BOOKS.

A DIGEST OF METABOLISM EXPERIMENTS IN WHICH THE BALANCE OF INCOME AND OUTGO WAS DETERMINED. BY W. O. ATWATER, PH.D., AND C. F. LANGWORTHY, PH.D. Bulletin No. 45 (Revised Edition). Washington: U. S. Department of Agriculture, Office of Experiment Stations. 434 pp.

This publication is a digest of about 3,600 experiments in which the balance of one or more of the factors of income and outgo was determined. It includes metabolism in both man and animals. The compilation has been prepared in connection with the work of the Office of Experiment Stations and, particularly, in connection with the investigations that are being pursued under the direction of Prof. Atwater, who is the special agent in charge of nutrition investigations. The compilation includes records, from the Russian literature and other sources, not found in general treatises and standard abstract journals. While the authors do not claim to have found all the investigations ever reported, they believe that comparatively few have escaped their attention.

An introductory chapter, containing a brief description of the compilation and a historical account of the subject, is followed by the experiments with man. These occupy three-fifths of the entire volume. Beginning with the nitrogen balance in healthy subjects, experiments on the influence of diet are first recorded, followed by those on the influence of other conditions. The experiments are numbered seriatim throughout the compilation. Each subject is treated separately. A table containing the data of the experiments is followed by a brief description of the objects and conclusions of each, together with other important information contained in the original publications.

After nitrogen metabolism in health are experiments on subjects in disease, arranged according to the classification of diseases in Osler's "Practice of Medicine." The experiments with man conclude with a description of those in which the balance of nitrogen and carbon was determined. In recording the experiments on animals, those on each animal are given collectively. At the end of the volume the names of experimenters and subjects are indexed separately.

The work shows that the literature has been extensively con-

sulted in its preparation and that this has been done with a thoroughness and intelligence essential to a valuable compilation of this kind. The arrangement of such material is difficult. While that presented in this volume has the disadvantage of separating some experiments that have a common interest, it appears to combine the greatest number of desirable qualities. The matter relating to each subject is well brought together in the index.

E. E. SMITH.

THE ARITHMETIC OF CHEMISTRY. BY JOHN WADDELL. New York: The Macmillan Co. 1899. viii + 133 pp. Price, 90 cents.

This is the best elementary text-book upon chemical arithmetic, or stoichiometry, we have yet examined. The general mistake made by most books of this class is to attempt too much and to explain too little. Formulas and rules are used too frequently, and too many problems are to be solved by simply substituting for a or b its numerical value. In Mr. Waddell's book the explanations are clear, and the laws upon which the solutions of the problems depend are plainly stated. The ground covered by the book is not extensive, but the most important chemical problems, such as the calculation of weights, the solution of chemical equations, the volume of gases, the calculations in volumetric analysis, the deduction of formulas from percentage composition, etc., receive a generous share of attention. Among the examples given for solution are many selected from the examination questions of the leading American and British colleges.

RICHARD K. MEADE.

BOOKS RECEIVED.

Bulletin No. 18. Sugar Beet Investigations in 1898. 24 pp. Bulletin No. 19. Miscellaneous Analyses (strawberries, peas, wines, foods, poisons, fertilizers, and potable waters). 24 pp. University of Idaho Agricultural Experiment Station, Moscow, Idaho. 1899.

A Short History of the Progress of Scientific Chemistry in Our Own Times. By William A. Tilden. London, New York, and Bombay: Longmans, Green & Co. 1899. x+276 pp. Price, \$1.50.

Die ätherischen Öle. Von E. Gildemeister und Fr. Hoffmann. Bearbeitet im Auftrage der Firma Schimmel & Co. in Leipzig. Mit vier Karten und zahlreichen Abbildungen. Berlin: Verlag von Julius Springer. 1899.

Report on Investigations to Determine the Cause of Unhealthy Conditions of the Spruce and Pine from 1880-1893. By A. D. Hopkins. 265 pp.

Commercial Fertilizers. By B. H. Hite and T. F. Watson. 12 pp. The Effect of Pressure in the Preservation of Milk. By B. H. Hite. 34 pp. West Virginia Agricultural Experiment Station, Morgantown, W. Va.

On the Associated Minerals of Rhodolite. By W. E. Hidden and J. H. Pratt. 6 pp. On the Occurrence, Origin, and Chemical Composition of Chromite. By J. H. Pratt. 6 pp. Reprinted from the *American Journal of Science*.

La Liquéfaction des Gaz. Méthods Nouvelles—Applications. Par J. Cauro. Paris: Gauthier-Villars, Imprimeur-Libraire. 1899. 83 pp.

School Chemistry. By Charles Baskerville, Ph.D., of the University of North Carolina. Richmond, Va.: B. F. Johnson Publishing Co. 1899. 159 pp. Price, 60 cents.

Easy Experiments of Organic Chemistry for Students' Laboratory Work. By John Howard Appleton. Providence, R. I.: Snow & Farnham. 1898. 107 pp. Price, 60 cents.

Saw Palmetto. By P. L. Sherman and C. H. Briggs. Reprinted from the *Pharmaceutical Archives*, 2, No. 6. 16 pp.

Commercial Fertilizers. Bulletin No. 82, Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky. 20 pp.

Alkali Studies, IV. By E. E. Slosson. Published as part of the Ninth Annual Report of the Wyoming Agricultural Experiment Station. July, 1899. Laramie, Wis. 29 pp.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE AGRICULTURAL EXPERIMENT STATION.]

A CONTRIBUTION TO THE CHEMISTRY OF BUTTER-FAT.¹

By C. A. BROWNE, JR.

Received June 28, 1899.

II. THE CHEMICAL COMPOSITION OF BUTTER-FAT.

WE have already spoken, in a somewhat general way, of those proximate components into which butter-fat is resolved by the process of saponification. The percentage of glycerol formed by the breaking up of the glycerides and the methods for its estimation were considered in a previous article.² We will confine ourselves, therefore, in the present paper to a study of the various fatty acids, both soluble and insoluble, as we obtain them from butter-fat, regarding also, to some extent, the combinations of these different acids with the glycerol base to form what we know as the glycerides, the mixture of which in varying proportions constitutes butter-fat itself.

There is no problem in analytical chemistry more difficult than that of making a quantitative separation of a mixture of different fatty acids. A mixture of two fatty acids is very hard to analyze, much more so a mixture such as we find in butter-fat where at least ten different acids are present. In a case of this kind the most that we can hope for is an approximation, since an exact quantitative separation is impossible in the present condition of analytical chemistry.

¹ Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

² This Journal, 21, 612.

Bearing this in mind it need not be thought strange that the analysis of the fatty acids from butter should be a subject upon which scarcely any two writers agree. Chemists are generally quite concordant in determinations of the saponification number and other common constants pertaining to butter-fat analysis ; it seems only reasonable, therefore, to attribute such discrepancies as we find in the percentages of the various acids to defective methods of analysis.

In the following table are given the percentages of the different acids in butter-fat according to several authorities :

TABLE V.

Acid.	1. Molt. ¹	2. Koefoed ²	3. Bell. ³	4 Blyth ⁴
Oleic.....	26.52	31.11	36.1	40.40
Stearic.....	40.93	1.83	49.46	47.50
Palmitic....	20.00	25.62		
Myristic.....		20.13	2.09	0.80
Lauric		7.32		
Capric	7.40	1.83	6.13	3.49
Caprylic.....		0.46		
Caproic		1.83		
Butyric		1.37		
Total	94.85	91.50	93.78	94.59

A difference in the composition of butter-fat itself no doubt explains to some extent the variations in the foregoing table ; a difference in composition, however, would hardly warrant such wide discrepancies as we observe between columns 1 and 2 in the case of stearic acid, or between columns 2 and 3 in the case of butyric acid.

A partial separation of the acids of butter into two fractions, one soluble in water and the other insoluble, is very easily effected, as has been shown ;⁵ the real difficulties of the work may be said to begin only with the final analysis of these two portions.

¹ König : *Nahrungs- u. Genussmittel*, second edition, p. 281. Original results expressed as glycerides were calculated to fatty acids.

² Koefoed : *Bulletin de l'Academie Royale Danoise*, 1891 ; Abstract in *Analyst*, No. 195, p. 130.

³ Bell : *Analysis and Adulteration of Foods*, Vol. II, 48. The fatty acids soluble in water were regarded as butyric acid ; the 2.09 per cent. of residual acids were soluble in hot water and had a combining weight of 136.

⁴ Blyth : *Foods ; Their Composition and Analysis*, fourth edition, p. 340.

⁵ This Journal, 21, 626.

To remove as far as possible the difficulties attending the presence of oleic acid, a butter-fat was selected which gave a rather low iodine absorption; the fat was examined first according to the ordinary methods of analysis and gave the following constants:

Saponification number.....	232.7
Ether number.....	232.5
Iodine number	29.28
Insoluble acids, per cent	86.40
Soluble " "	8.35
Saponification number of insoluble acids.....	215.5
Molecular weight " " " ..	260.3
Saponification number " soluble " ..	572.5
Molecular weight " " " ..	98.0

One hundred grams of the butter-fat were taken and the soluble and insoluble acids obtained by methods already described. It is an interesting and well-known fact that in the natural fats only acids exist that have an even number of carbon atoms.¹ Besides the acids mentioned in Table V there have been found in butter-fat oxy-acids,² and also acetic and arachidic acids;³ the two latter, however, occur in such minute quantities that their presence is not worth considering.

ANALYSIS OF THE INSOLUBLE ACIDS.

The two methods most generally followed by chemists for effecting a separation of a mixture of insoluble acids are that of fractional distillation and that of fractional precipitation. In our work the latter method was selected, since it seemed to offer fewer difficulties and fewer sources of error; we have never given the distillation method a fair trial, but a few experiments seemed to indicate that there was an insufficient range in the character of the different fractions and that the whole process was attended with danger of decomposition.⁴

In making the fractional precipitations the method of Heintz⁵ was for the most part followed.

The insoluble acids (86.4 grams), obtained from 100 grams of

¹ Richter's Organic Chemistry, Smith's translation of fourth German edition, p. 186.

² Bondzynski and Ruß: *Ztschr. anal. Chem.* (1891), 1.

³ Benedikt: *Analyse der Fette*, third edition, p. 544.

⁴ Koefoed (*Vid. op. cit.* this article, p. 808), however, seems to have used the distillation method with some degree of success.

⁵ Heintz: *J. prakt. Chem.*, 66, 1.

butter-fat, were dissolved in ninety-five per cent. alcohol, using such a quantity that nothing crystallized out at 25° C. The solution was then cooled to zero, and after several hours, when crystallization was complete, filtered through a funnel kept cold by means of an ice-jacket. The precipitate of fatty acids, consisting of a white crystalline mass, we will designate as Portion I, and the acids contained in the filtrate as Portion II.

Portion I contained, besides other acids, a small quantity of oleic acid held back mechanically; to remove as much as possible of this, the precipitate of acids was dissolved in a small quantity of hot alcohol, recrystallized in the cold, and filtered as before, the filtrate being added to Portion II.

Portion I was again dissolved in about 500 cc. of hot alcohol, cooled in ice-water, and after recrystallization filtered through the ice-funnel; the precipitate constituted Part 1. The filtrate from Part 1 was evaporated to about 300 cc., cooled in ice-water, and the fat acid crystals filtered off as before; the precipitate constituted Part 2. The filtrate from Part 2 was evaporated to about 150 cc., and the process continued for one more crystallization, Part 3 being obtained; the filtrate from Part 3 was added to Portion II.

The different Parts, 1, 2, and 3, of Portion I were then washed with ether into weighed beakers; after evaporating the ether the acids were dried for a short time at 100°, after which they were cooled, weighed, and preserved for further examination.

Portion II was treated with 100 cc. of a five per cent. solution of magnesium acetate in alcohol, cooled to 0° C., and after crystallization of the magnesium salts was complete, filtered. The precipitate, Part *a*, was washed with 100 cc. of the alcoholic magnesium acetate and the washings added to the original filtrate. The filtrate from Part *a* was then rendered alkaline with ammonia and subjected to a second crystallization at 0° C., when a second precipitate, Part *b*, was obtained; this was filtered off and washed similarly to Part *a*. Nothing more separating from the filtrate at zero, the solution was treated again with ammonia until strongly alkaline; 100 cc. more of the magnesium solution were added and the liquid allowed to stand in the cold for twenty-four hours. The precipitate thus obtained was collected on a

filter and washed with small amounts of the alcoholic magnesium solution; it constituted Part *c*.

The three fractions of Portion II, Parts *a*, *b*, and *c*, consisting of the magnesium soaps, were then decomposed with dilute hydrochloric acid, and the liberated acids thoroughly washed with hot water to remove all traces of magnesium. The fatty acids from each fraction were then washed with ether into weighed beakers, and, after evaporation of the ether, dried for a short time at 100°, when they were cooled, weighed, and preserved for further examination.

In the analysis of the different fractions from Portions I and II, the saponification number and iodine absorption were determined; from the former constant the mean molecular weight of the mixture of fatty acids is calculated¹ and from the latter the amount of oleic acid in each fraction is determined:² the oleic acid, though sometimes present in but minute quantities, must, nevertheless, be considered in the analysis of the several fractions.

Some uncertainty prevails as to the accuracy of calculating the percentage of oleic acid in a mixture of glycerides or fatty acids from the iodine number alone. There is not only the possibility of other unsaturated acids existing besides oleic acid, but also the danger that iodine may be substituted as well as added in the course of the reaction. These objections are no doubt valid in the case of many vegetable and fish oils, but apply with less force to the common fats of animal origin, which contain, so far as known, only one unsaturated acid; *viz.*, oleic.

The possibility of iodine being substituted, with the glycerides or acids of butter-fat at least, appears to us to be very slight; after removing the olein or oleic acid by repeated crystallizations of the fat or fatty acids, the percentage of iodine absorbed can be reduced practically to nothing, thus showing that with the higher saturated glycerides and acids but very little, if any, substitution occurs.

We have selected as the first step in the calculations the de-

¹ By the formula $M = \frac{56100}{S}$. Benedikt: *Analyse der Fette*, third edition, p. 163.

² By the formula $O = \frac{100}{90.07} I = 1.1102 I$, 90.07 being the theoretical iodine absorption of pure oleic acid. Benedikt: *Ibid.*, p. 173.

termination of the mean molecular weight of the fatty acids in each fraction after deducting the oleic. This result is obtained by the following formula :

$$\frac{100}{m} - \frac{O}{282} = \frac{100-O}{x};$$

or

$$x = \frac{282 m (100-O)}{28200-mO}.$$

O = percentage of oleic acid as calculated from iodine number.

m = mean molecular weight of original acids.

x = " " " after deducting oleic.

If now we assume that there are not more than two acids present in each fraction besides the oleic and that these acids are adjacent homologues of even carbon atoms, then the relative percentage of each acid can be determined from the following formulas :

$$x + y = 100;$$

$$\frac{x}{m_1} + \frac{y}{m_2} = \frac{100}{m};$$

from which

$$x = \frac{100 m_1 (m-m_2)}{m (m_1-m_2)};$$

$$y = \frac{100 m_2 (m_1-m)}{m (m_1-m_2)}.$$

m = mean molecular weight of the two acids.

m_1 and x = molecular weight and percentage, respectively, of the higher acid.

m_2 and y = molecular weight and percentage, respectively, of the lower acid.

The expression m_1-m_2 for the saturated fatty acids of even carbon atoms equals 28; substituting this value in the previous equations :

$$x = \frac{100 m_1 (m-m_2)}{28 m};$$

$$y = \frac{100 m_2 (m_1 - m)^1}{28 m}$$

To ascertain what acids are present in any particular fraction, it is only necessary to observe between what two homologues the mean molecular weight of the fraction falls, after deducting the oleic.

The formulas, as derived from the two preceding general equations, for calculating the percentage of stearic acid (*S*) and palmitic acid (*P*) in a mixture of the two, knowing the mean molecular weight (*m*), are as follows :

$$S = \frac{28400 (m - 256)}{28 m} ;$$

$$P = \frac{25600 (284 - m)}{28 m} .$$

In the same way for palmitic acid (*P*) and myristic acid (*M*) :

$$P = \frac{25600 (m - 228)}{28 m} ;$$

$$M = \frac{22800 (256 - m)}{28 m} .$$

The analytical data of the various fractions belonging to Portions I and II, together with the calculated amounts of the different acids, are given in the following table :

¹ There is some difference among chemists as to the proper formula to use for calculating the percentage of two acids from the mean molecular weight. Benedikt, Hehner, and the majority of German chemists take the formula $\frac{x}{m_1} + \frac{y}{m_2} = \frac{100}{m}$, while the calculations of Allen, Prescott, and many others are based upon the formula $xm_1 + ym_2 = 100m$. The former formula seems to us the only correct one. To take for example a simple case :

	Per cent.
1 molecule stearic acid weighs 284	= 52.59
1 " palmitic " " 256	= 47.41
2 molecules of mixture weighs	540 = 100.00
Mean molecular weight of mixture	= $\frac{540}{2}$ or 270.

If we determine now from the two formulas, what percentages of stearic and palmitic acids will give a mean molecular weight of 270, we obtain 52.59 per cent. stearic and 47.41 per cent. palmitic, the theoretical results, by the formula $\frac{x}{m_1} + \frac{y}{m_2} = \frac{100}{m}$; whereas the formula $xm_1 + ym_2 = 100m$ gives exactly fifty per cent. of each.

TABLE VI.

	Portion I.			Portion II.			Total per cent.
	Part 1.	Part 2.	Part 3.	Part a.	Part b.	Part c.	
Weight of fraction.....	5.20 grams	6.01 grams	21.13 grams	9.22 grams	7.82 grams	5.05 grams
Mean molecular weight of fraction.....	272.2	260.0	260.7	254.6	254.5	251.2
Iodine number of fraction.....	3.44	10.94	15.03	8.41	19.85	25.12
Per cent. oleic acid in fraction.....	3.82	12.14	16.68	9.34	22.03	27.88
Mean molecular weight after deducting oleic	271.8	257.2	256.8	252.1	247.7	241.0
Weight of stearic acid	2.95 ¹ grams	0.25 gram	0.56 gram	3.76
" " palmitic "	2.05 grams	5.03 grams	17.05 grams	7.32 grams	4.44 grams	1.79 grams	37.68
" " myristic "	1.05 grams	1.66 grams	1.85 grams	4.56
Undetermined.....							7.90 ²

¹ Contains also the oxy-acids, a correction for which will be introduced later.² Found by subtracting the sum of the acids determined and the oleic acid 32.50 per cent. (calculated from iodine absorption) from 86.40, the total per cent. of insoluble acids.

The 7.90 per cent. of undetermined acids, which escaped precipitation, includes all of the lauric acid and no doubt a considerable part of the myristic; the percentage of each of these acids can be arrived at in another way. Having five members present in a mixture of fatty acids and knowing the molecular weight and percentage of three of them, the mean molecular weight of the other two can be determined by the following formula :

$$\frac{a}{m_1} + \frac{b}{m_2} + \frac{c}{m_3} + \frac{100 - (a + b + c)}{x} = \frac{100}{m}.$$

a , b , and c are the percentages of the three known acids and m_1 , m_2 , and m_3 their respective molecular weights. m is the mean molecular weight of the whole mixture and x the mean molecular weight of the two acids sought.

Applying this formula to the case in hand we have for the three known acids, oleic, stearic, and palmitic, the following percentages :

TABLE VII.

	In 100 parts of butter-fat.	In 100 parts of acids.
Oleic acid (from iodine number)	32.50	37.61
Stearic acid	3.76	4.35
Palmitic acid	37.68	43.61
Myristic and lauric acids	12.46	14.43
Total	86.40	100.00

The mean molecular weight of the insoluble fatty acids from the butter was 260.3; substituting these values in the formula we obtain the following equation :

$$\frac{37.61}{282} + \frac{4.35}{284} + \frac{43.61}{256} + \frac{14.43}{x} = \frac{100}{260.3};$$

$$\text{or } 0.13339 + 0.01532 + 0.17035 + \frac{14.43}{x} = 0.38418;$$

$$\text{or } \frac{14.43}{x} = 0.06512;$$

$$\text{whence } x = 221.6.$$

This figure for the mean molecular weight falling between 200

¹ Strictly the formula should also take into account the oxy-acids; this, however, would make no difference with the final results, inasmuch as the mean molecular weight of the determined acids (and hence of the undetermined) would remain the same in either case.

and 228 would indicate a mixture of lauric and myristic acids. Knowing the mean molecular weight (m) of a mixture of myristic (M) and lauric (L) acids, the percentages of each may be calculated from the formulas

$$M = \frac{22800(m-200)}{28m},$$

$$L = \frac{20000(228-m)}{28m}.$$

Substituting the value 221.6 for m in the preceding equations we obtain 79.37 per cent. myristic and 20.63 per cent. lauric acid; this would give in the 12.46 parts of undetermined acids 9.89 parts of myristic and 2.57 parts of lauric acid for 100 parts of butter-fat.

Such a method for analyzing a mixture of fatty acids as the one described manifestly presents many crudities; the method of Heintz, however, "supplies the only means of obtaining an insight into a mixture of non-volatile acids."¹ Unfortunately, "there is no practical method of proving that two and only two acids are present" in any particular fraction, and therein lies the principal fault of the method. Allen observes that "as a rule if the mixed fatty acids be divided into a sufficient number of fractions, each fraction will contain only two homologues,"² and this assumption seems to be a fairly reasonable one.

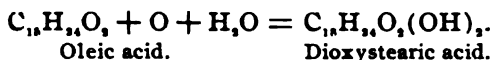
The oleic acid is a disturbing factor throughout the whole process and its presence must be taken into account in the analysis of the different fractions. We believe too little attention has been paid to this point. The method could be improved greatly if there were some good means of removing the oleic acid at the beginning of the process. The plan of converting the mixture of acids into the lead soaps and removing the lead oleate with ether would not work well on a large quantity of acids, and besides this the process does not effect a perfect separation.

We have taken no account thus far of the oxy-fat acids: that such acids are present in butter-fat seems certain from the acetyl figure which the insoluble acids always give. The oxy-acids probably do not exist in the fat as it is secreted from the lacteal

¹ Hehner and Mitchell: *Analyst*, No. 249, p. 317.

² Commercial Organic Analysis, third edition, Vol. II, Part 1, p. 242.

glands, but are later oxidation products of the oleic acid—dioxystearic¹ acid being no doubt principally formed.



Owing to the low solubility of the higher oxy-acids in cold alcohol, any oxy-acids present would come down with the first crystallization (Part I, Table VI), and this fact would alter somewhat the percentages of the acids in this fraction.

Benedikt has devised a formula by means of which the percentage of an oxy-acid in a mixture of fatty acids can be calculated from the acetyl number, provided that the constitution and molecular weight of the oxy-acid is known. The equation is

$$x = \frac{100 \, c \, m}{a(56100 - 42c)},$$

in which c = the acetyl number.

a = the number of hydrogen atoms in the oxy-acid replaceable by acetyl.

x = percentage sought of the oxy-acid having a molecular weight m .

Applying this formula to the insoluble acids from the average butter-fat having an acetyl number of 4.1 we would obtain for dioxystearic² acid 1.16 per cent., or calculated to the original butter-fat 1.00 per cent. of oxy-acid.

There are no doubt other oxy-acids present besides the dioxystearic in the mixture of insoluble acids, so that the results from this method of calculation can only be considered approximate. The percentage of oxy-acids in butter-fat increases with time and is therefore never a fixed quantity. The gradual increase in the acetyl number, together with the decrease in the saponification number of the insoluble acids, with the age of a butter-fat, goes to show that oxy-acids of a high molecular weight are continually being formed. This fact will be explained more fully under the subject of "Rancidity in Butter-fat."

If we introduce a correction for the percentage of oxy-acid, as found, in the first fraction of the insoluble acids and recalculate

¹ A Scala (*Staz. sperim. agr. Ital.* (1897), p. 613, shows that this acid is formed among the oxidation products of oleic acid.

² Benedikt: *Monatsh. Chem.* (1890), 95, and *Analyse der Fette*, third edition, p. 178.

³ For dioxystearic acid in the formula $a = 2$ and $m = 316$.

the stearic and palmitic acids, the analysis of Part I would then be :

	Grams.
Dioxystearic acid.....	1.00
Stearic acid.....	1.02
Palmitic acid.....	2.98

The complete analysis of the insoluble acids from 100 parts of butter-fat accordingly would be :

	Grams.
Dioxystearic acid	1.00
Oleic acid	32.50
Stearic acid	1.83
Palmitic acid.....	38.61
Myristic acid.....	9.89
Lauric acid.....	2.57
Total	<hr/> 86.40

A noteworthy fact in connection with the above results is the low percentage of stearic acid in butter-fat. This is somewhat contradictory to the statements which we find given by many authorities on the subject who regard stearic as one of the principal acids in butter-fat, it being placed, by some writers, as high even as forty per cent. We believe that these statements should be modified somewhat; when we consider that oleic acid of molecular weight 282 constitutes over one-third of the insoluble acids from butter-fat, it is self-evident that the percentage of stearic acid of molecular weight 284 must be small in comparison with that of its lower homologues, to give a mean molecular weight of 261 to the whole mixture.

Koefoed,¹ in his analysis of butter-fat, obtained only 1.83 per cent. stearic acid which, by a strange coincidence, is exactly the same quantity found by us after correcting for the oxy-acids.

Hehner² and Mitchell, by removing the oleic and lower insoluble acids with dilute alcohol and analyzing the residue, obtained only from one and three-tenths to three and six-tenths per cent. stearic acid; the same authorities, with their process³ of removing all other acids by treatment of the insoluble acids at 0° C. with a saturated solution of stearic acid in alcohol,

¹ *Vid. op. cit.*, p. 808 of this article.

² *Analyst*, No. 249, p. 321.

³ *Ibid*, p. 322.

obtained in over 100 determinations only minute quantities of stearic acid and in many cases none at all.

This low percentage of stearic acid should rank with the high percentage of soluble fatty acids, as one of the characteristic differences between butter and other animal fats.

ANALYSIS OF THE SOLUBLE ACIDS.

A great many methods have been devised for the analysis of a mixture of the lower soluble fatty acids, but very few of them seem practicable in actual work. The method of fractional distillation, which suggests itself perhaps first of all, does not give good results when working with a small quantity of acids, the principal difficulty which we have found being that of not securing a wide enough range in the character of the several fractions.

No more satisfactory were the methods based upon the difference in the chemical affinities of the various acids.¹ A neutralized solution of the mixed soluble acids was decomposed with successive portions of tenth-normal sulphuric acid, the liquid being subjected to distillation after each addition of acid. The various distillates were neutralized with tenth-normal barium hydroxide and the mean molecular weights of the acids in each fraction determined. A difference was found in the acids of the several successive distillates, but not a distinctive one, the several molecular weights varying only from two to three units. The theory of the method is borne out, but imperfectly. In one experiment the mean molecular weight of the acids in the first fraction was 102.7; the succeeding fractions gave in their order 99.4, 96.8, 94.8, 93.9, 91.2, and 88.7. It is seen that the mean molecular weights of the acids in the successive distillates decrease until we have practically pure butyric acid in the final fraction; the differences are too small, however, to form any basis for calculations.

The method of Duclaux,² based upon the difference in ratio of vaporization of the various acids from their solution, did not appear adaptable to the present instance where more than two acids were present.

The following method, worked out by the writer, was found

¹ Allen : *Commercial Organic Analysis*, third edition, Vol. I. p. 487.

² Duclaux : *Ann. Chem. Phys.* [5], 11, 233.

to give a considerable range in the character of the different fractions, with but little trouble of execution; it is based upon the difference in the solubility¹ of the various lower homologues in water at different temperatures.

One gram of the mixed acids is weighed out into a small fifty cc. flask and treated with twenty-five cc. of distilled water, previously cooled to nearly 0° C. The flask is placed in a beaker of ice and agitated frequently for about five minutes; the contents of the flask are then poured into a small filter placed in a funnel surrounded by ice, and the flask rinsed out with small portions (five cc.) of the cold water, the rinsings being poured upon the filter and allowed to run into the beaker holding the original filtrate. Not more than twenty-five cc. of water are used for the washing. The acids left on the filter are washed back into the flask with about twenty-five cc. of distilled water at 30° and, after being kept at this temperature for five minutes with frequent shaking, again filtered. The flask is rinsed out and the acids on the filter washed as before with small quantities of water (about twenty-five cc. in all) at 30°, the combined filtrate and washings constituting Fraction 2. The acids remaining on the filter are then treated successively in the same manner with water at 60° and 95°, Fractions 3 and 4 being thus obtained.²

The various fractions are next titrated with standard tenth-normal barium hydroxide, using phenolphthalein as indicator; the solutions of the barium salts are evaporated to dryness in weighed platinum dishes, and the residues dried to constant weight at 100°. From the weight of the residue and the weight of barium oxide contained therein, the mean molecular weight of the acids in each fraction is determined.³ The amount of barium oxide in the residue can be calculated either from the volume of solution used to neutralize the acids, or by igniting

¹ Storer (Dictionary of Chemical Solubilities) gives the following:

Butyric acid soluble in water in all proportions:

Caproic acid	soluble in	96	parts of water at	7° C.
Caprylic "	"	400	"	100° C.
Capric "	"	1000	"	20° C.

² The physical characters of the acids are observed to change during the process of washing. After the removal of the first fraction the acids lose their mobility and acquire a thick, oily consistency. The strong rancid smell, characteristic of butyric acid, entirely disappears with the removal of the second fraction, while the residual acids possess a very peculiar odor, resembling somewhat that of perspiration.

³ This Journal, 21, 628.

the residue with sulphuric acid and weighing the barium sulphate.

In one experiment, conducted by the method just described, there were found for the different fractions the following results:

TABLE VIII.

Temperature of water used for washing.		Mean molecular weight of acids.
Fraction No. 1.....	5° C.	91.4
" " 2.....	30° C.	113.1
" " 3.....	60° C.	123.6
" " 4.....	95° C.

The quantity of acids left after treating with water at 60° amounted to only a few milligrams and so was insufficient for an accurate molecular weight determination.

The weight of acids in each fraction can be found from the formula

$$W = \frac{Mn}{10,000},$$

in which W equals the weight in grams of acids, M the mean molecular weight of the acids, and n the number of cubic centimeters of tenth-normal alkali used for their neutralization.

If we assume that only two acids are present in each fraction, an assumption¹ probably not very far from true, the percentage of each acid can be calculated from the mean molecular weight according to the general formulas already given. For a mixture of butyric (B) and caproic (C) acids,

$$B = \frac{8800(116-m)}{28m};$$

$$C = \frac{11600(m-88)}{28m}.$$

For a mixture of caproic (C) and caprylic (C_1) acids,

$$C = \frac{11600(144-m)}{28m};$$

$$C_1 = \frac{14400(m-116)}{28m}.$$

¹ The wide difference in the solubility of the lower acids in water would almost preclude the possibility of finding more than two acids in each fraction. There is, however, this possibility, which experiments would seem to indicate, that the solubility of the higher acids in water is somewhat greater if lower acids are present. This is a point well worth investigation.

Several analyses of the soluble acids from butter-fat conducted by the method described gave the following average composition :

	Per cent.
Butyric acid.....	65.28
Caproic "	25.00
Undetermined.....	9.72

The mean molecular weight of the undetermined acids can be calculated from the equation,

$$\frac{65.28}{88} + \frac{25.00}{116} + \frac{9.72}{x} = \frac{100}{98},$$

from which $x = 154$. This value, falling between 144 and 172, would indicate that the undetermined acids consisted of caprylic and capric. From the mean molecular weight (m) the percentages of caprylic (C_1) and capric (C_2) acids can be calculated as follows :

$$C_1 = \frac{14400 (172 - m)}{28 m};$$

$$C_2 = \frac{17200 (m - 144)}{28 m}.$$

In the undetermined residue of 9.72 per cent. we find from the above formulas sixty parts of caprylic and forty parts of capric acid, or 5.83 per cent. caprylic and 3.89 per cent. capric in the total mixture of soluble acids.

Calculating the analysis to the 8.35 per cent. of soluble acids in the original butter-fat we obtain :

	Per cent. ¹
Butyric acid.....	5.45
Caproic "	2.09
Caprylic "	0.49
Capric "	0.32
Total.....	8.35

¹ In connection with these percentages for the soluble acids it will be of interest to quote the results of two French chemists :

Duclaux (*Compt. rend.*, 102, 1022) found in eight samples of butter examined 3.38 to 3.60 per cent. butyric and 2.08 to 2.26 per cent. caproic acid. Violette (*Compt. rend.*, 111, 345) found for good butter 5.32 to 6.06 per cent. butyric and 3.22 to 3.66 per cent. caproic acid. Apparently no attempts were made by either of these chemists to determine the caprylic and capric acids.

For other results see Table V.

SUMMARY.

The results of the analysis of the mixed acids from the butter-fat examined, together with the equivalent percentages of triglycerides, are given in the following table :

TABLE IX.

Acid.	Percentage of acid.	Percentage of triglycerides.
Dioxystearic.....	1.00	1.04
Oleic	32.50	33.95
Stearic	1.83	1.91
Palmitic.....	38.61	40.51
Myristic	9.89	10.44
Lauric.....	2.57	2.73
Capric.....	0.32	0.34
Caprylic.	0.49	0.53
Caproic.....	2.09	2.32
Butyric.....	5.45	6.23
Total.....	94.75	100.00

Other bodies, such as coloring-matter, lecithin, cholesterin, phytosterin, etc., which occur in butter-fat in only minute quantities, have not been considered in the above analysis. These substances go to make up the unsaponifiable matter of butter-fat, the total amount of which we have found to be only about one-tenth per cent.

We have made an elementary analysis of butter-fat and find the agreement between the actual percentages of carbon, hydrogen, and oxygen, and the theoretical figures as calculated from the percentages of the various glycerides in the preceding table, to be very close.

	Carbon.	Hydrogen.	Oxygen.
Actual	75.17	11.72	13.11
Theoretical	74.86	11.71	13.43

The close agreement between these two sets of results would indicate that the figures expressing the percentages of acids and glycerides in Table IX are not very far removed from the truth.

THE GLYCERIDES OF BUTTER-FAT.

Experiments of Bell,¹ Blyth,² and other chemists indicate that there are certain glycerides in butter-fat of a complex nature ;

¹ Allen : Commercial Organic Analysis, third edition, Vol. II, Part 1, p. 180.

² Blyth : Foods; Their Composition and Analysis, fourth edition, p. 340.

that instead of simply one acid we may have two or even three different acid radicals in the same molecule.

If a mixture of tributyrin, tripalmitin, and triolein be prepared and treated with alcohol, it is possible to extract the tributyrin completely. With butter-fat, on the other hand, such an extraction cannot be made, a fact due without doubt to the butyric acid being combined with certain higher fat acids to the same glycerol radical.¹ In confirmation of this, Blyth and Robertson² have isolated from butter-fat a crystalline glyceride of the formula



a mixed ester of butyric, palmitic, and oleic acids.

While a part of the butyric, palmitic, and oleic acids in butter-fat is no doubt bound up together in one molecule, it is also certain that these acids exist in glycerides of a different nature. Experiments seem to indicate that there are present glycerides which contain at least two radicals of one acid in the same molecule and probably three. Tripalmitin certainly exists and has been isolated by us in a state of comparative purity. The separation of all the various glycerides is a problem at present beyond the power of the chemist. It is only possible to make a few rough separations and from certain analytical data draw some general conclusions.

If a melted butter-fat is allowed to stand for some time at about 25° C., a crystalline deposit will separate out. By filtering we obtain two portions,—a clear transparent oil, the so-called butter-oil, and a solid mass comprising all the glycerides of higher melting-point. If the butter-oil is cooled another deposit will form; by repeating the process of filtering and cooling, the congealing-point of the oil can be reduced from 25° C. to below 10° C. These different fractions of oil will be found to differ in chemical as well as physical properties, as can be seen from the following table:

TABLE X.

Congeaing-point.	Iodine number.	Saponification number.
25° C.	35.05	233.0
12° C.	39.24	234.0
9° C.	40.95	235.6

¹ Beredikt: *Analyse der Fette*, third edition, p. 544.

² *J. Lond. Chem. Soc.*, Proceedings (1889), 5

The increase in the iodine and saponification numbers, as the congealing-point decreases, is due to an increase in the percentages of oleic and the soluble acids. The quantity of soluble acids increases much faster than the saponification number indicates, since the increase in oleic acid tends to keep this constant down.

The butter-oil of 9° congealing-point contains, according to its iodine absorption, over forty-five per cent. oleic acid, which quantity is considerably in excess of the percentage required by such a glyceride as that of Blyth and Robertson. Indications would point to the presence of glycerides containing at least two radicals of oleic acid in the molecule, and there is no reason to doubt the existence of triolein itself.

The solid mass left on the filter, after removing the butter-oil, still contains a high percentage of oleic acid; it resembles butter-fat itself in outward appearance. The body is somewhat harder, however, than butter-fat, possessing also a higher melting-point and lower content of soluble acids. For want of a better name, we have termed this residue, left after removing the oil, *butter-palmitin*. The relation between the constants of butter-oil, butter-palmitin, and the original butter-fat can be seen from the following table :

TABLE XI.

	Melting-point.	Saponification number.	Iodine number.	Reichert number.
Original butter-fat	33°	231	31.00	15.30
Butter-oil.....	25° ¹	233	35.05	18.18
Butter-palmitin.....	38°	228	27.66	11.23

By subjecting the butter-palmitin to repeated crystallizations from some suitable solvent (chloroform was found to be the best), it is possible to remove practically all of the oleins and lower glycerides and to obtain almost pure tripalmitin itself. The body possesses a beautiful, white, flaky appearance, crumbles readily between the fingers, and leaves no oily spots when spread on paper. Traces of oleic, stearic, and lower soluble acids are generally present as impurities. A specimen of the glyceride gave a saponification number of 207; the saponification number of tripalmitin, according to theory, is 208.

¹ Congealing-point.

If we treat butter-fat with hot ninety-five per cent. alcohol, then cool, filter, and evaporate the alcohol, a small quantity of a gum-like fat is left. A body so obtained melted at $22.5^{\circ}\text{C}.$, gave a saponification number of 257, an iodine number of 26.15, and yielded about seventy-nine per cent. insoluble and fourteen per cent. soluble acids. The small percentage of the body obtained and its high saponification number (higher than that required for an oleopalmitobutylin), would point to glycerides containing more than one radical of the lower acids.

In conclusion, the most that we can say is that, while the evidence is strongly in favor of the existence of complex glycerides, there are equally good reasons for believing in the existence of simpler bodies. An analysis of the fatty acids from the different fractions of the butter-oil and butter-palmitin would throw much light upon the constitution of the glycerides contained therein; for such work, however, our time has been too limited. We hope, if possible, in the future to continue our work in this direction.

NOTE.

Inasmuch as the reliability of the analyses, contained in the foregoing paper, is dependent to a great extent upon the accuracy of certain chemical methods, a word should be said in regard to the extent of error which is involved in work of the latter kind.

Nearly all of the calculations concerning molecular weights and percentages were based upon the determination of two constants, the saponification number and iodine absorption. Wherever possible, duplicate, and in some cases triplicate, determinations of these constants were made. The difference between two determinations of the saponification number rarely exceeded ± 1 , and the error between duplicate determinations of the iodine absorption was seldom greater than ± 0.1 ; these differences would affect only slightly the calculation of the mean molecular weights and percentages.

In standardizing the different solutions used for the volumetric work we have employed a few methods, which for speed and accuracy we think superior to some other processes in more general use; we will therefore mention them briefly in this connection.

Tenth-normal barium hydroxide is standardized by evaporating a measured quantity (twenty to fifty cc.) in a weighed platinum dish with a slight excess of dilute sulphuric acid, igniting the residue, and weighing the barium sulphate.

Tenth-normal sulphuric acid is standardized in a similar way. Twenty cc. of the acid are measured from a burette into a weighed platinum dish and the solution carefully neutralized with tenth-normal barium hydroxide, using phenolphthalein as indicator; the liquid is evaporated to dryness, the residue ignited, and the weight of barium sulphate determined. The weight of barium sulphate found divided by 0.2335 will give the factor for the tenth-normal sulphuric acid. In this way the barium hydroxide and sulphuric acid can both be standardized by a single operation. Determinations can be made in one-fourth less time by this process than by the usual method of precipitation and with no difference as regards accuracy of results. The barium hydroxide used should be perfectly pure and free from other alkali; if not C. P. it can be easily purified by recrystallization.

The two tenth-normal solutions just mentioned can be used for standardizing the half-normal alcoholic potash and half-normal hydrochloric acid employed for determining saponification numbers. Another method, which we have been accustomed to apply as a check, has proved very successful in the case of standardizing these last-named solutions.

Ten cc. of the half-normal potash solution are carefully neutralized with the half-normal hydrochloric acid, using phenolphthalein, and the number of cubic centimeters used carefully noted; the liquid, after evaporating off the alcohol, is diluted to about fifty cc. and an excess of platinic chloride solution added. The potassium platinichloride is precipitated and determined in the usual way, a Gooch crucible being used for collecting the precipitate. The weight of potassium platinichloride divided by 1.2145 will give the factor for the half-normal alcoholic potash solution; from the number of cubic centimeters of the acid used to neutralize the potash the factor for the half-normal hydrochloric acid is found. Factors obtained for the half-normal solution by precipitation with platinic chloride and by titration against the tenth-normal solutions have always showed a very close agreement.

HALIDES AND PERHALIDES OF THE PICOLINES.

BY PAUL MURRILL.¹

Received June 19, 1890.

THE history of the periodides has been given in papers previously published from this laboratory,² and work upon various phases of the problem has been in progress here since 1895.³ For our present knowledge of picoline we are chiefly indebted to the labors of Anderson,⁴ Baeyer,⁵ Dewar,⁶ and Ramsay.⁷ This research was undertaken as an extension of the work of Prescott and Trowbridge on pyridine and quinoline, and for the purpose of studying the homologues in the series, inasmuch as the presence of a side-chain can be considered as being a step nearer to the composition of the vegetable alkaloid.

EXPERIMENTAL PART.

I. NORMAL IODIDES.

α-Picoline Methyl Iodide, $C_6H_7(CH_3)N.CH_3I$.—This compound was prepared and described by Ramsay⁸ in 1876, and the same method of preparation was used. Picoline and methyl iodide unite readily at ordinary temperatures with evolution of heat, so that a reflux condenser is necessary to prevent loss of methyl iodide. The product soon solidifies to a yellowish mass, and is recrystallized from absolute alcohol, from which solvent it comes out in long white needles, melting at 224° (Ramsay 227°).

	Calculated for $C_6H_7N.CH_3I$.	Found.
Iodine	53.97	53.5 ⁹

The isomeric *β*- and *γ*-compounds were not obtained pure but

¹ A thesis presented to the council of the graduate school of the University of Michigan, for the Degree of Doctor of Philosophy, June, 1899.

² A. B. Prescott: The Periodides, this Journal, 17, 775 (1895); Periodides of the Alkaloids, *Pharm. Review*, 14, 172 (1896).

³ Prescott and Trowbridge: Periodides of Pyridine, this Journal, 17, 859, and 19, 322; Trowbridge and Diehl: Halides and Perhalides of Pyridine, this Journal, 19, 558; Trowbridge: Perhalides of Quinoline, this Journal, 21, 66; Gomberg: Perhalides of Caffeine, this Journal, 18, 347; Prescott and Gordin, Alkaloidal Periodides, this Journal, 20, 706.

⁴ *Ann. Chem.* (Liebig), 60, 86 (1846); 70, 32 (1849); 80, 44 (1851); 94, 358 (1855); *Edinb. Phil. J.*, 146 and 291 (1846); *Phil. Mag.*, (3), 33, 174 and (4), 9, 291.

⁵ *Ber. d. chem. Ges.*, 2, 398 (1869).

⁶ *Chem. News*, 23, 38 (1871).

⁷ *Phil. Mag.*, (5) 2, 269 (1876); 4, 241 (1877); 6, 19 (1878); *Ber. d. chem. Ges.*, 11, 1836.

⁸ *Phil. Mag.*, (5), 2, 277.

⁹ For methods of analysis see last part of this paper.

the results show that their melting-points are in all probability considerably lower than that of the α -compound. Five grams of picoline boiling at 137° – 140° (the last fraction of a 400 grams lot) were converted into the methiodide and crystallized once from absolute alcohol. These crystals appeared to be a mixture of two or more kinds, and melted at 183° . It was further converted into the triiodide described further on, and in view of later facts appears to have been a mixture of the α - and γ -compounds. A mixture of the α - and β -compounds was obtained as an oil, and this was also used in the preparation of periodides.

α -Picoline Ethyl Iodide, $C_6H_7N.C_2H_5I$.—This compound was prepared by Anderson¹ in 1855, and by him the melting-point is said to be below 100° , but is not definitely stated. He prepared it by heating picoline and ethyl iodide in a sealed tube, but this has been found to be unnecessary, and instead the constituents were heated on a water-bath under reflux condenser. The reaction is complete in two hours; and on cooling the oil solidifies to a yellowish mass. The excess of ethyl iodide is distilled off, and the residue dissolved in hot absolute alcohol. When cooled slightly, ether is added as long as the precipitate redissolves on shaking, and then it is allowed to crystallize. From this it comes out in large feathery plates, colorless or faintly yellow. It melts at 123° , and contains 50.8 per cent. iodine; theory 50.93 per cent.

Picoline Propyl Iodide, $C_6H_7N.C_3H_7I$.—Prepared by heating the constituents on the water-bath under reflux condenser. The action is complete in about two hours, and a thick sirup is formed, which solidifies to a crystalline mass on cooling. A portion was dried on porous plates in a desiccator, and the remainder crystallized from a very small amount of hot absolute alcohol. Yellowish needles formed, melting at 77° .

	Calculated for $C_6H_7N.C_3H_7I$.	Crude.	Found. Crystallized.
Iodine	48.23	45.2	48.3

Picoline Isopropyl Iodide, $C_6H_7N.C_3H_7I$.—Prepared in same manner as preceding, using instead isopropyl iodide. Needles which melt at 142° , and contain 48.4 per cent. iodine.

Picoline Butyl Iodide, $C_6H_7N.C_4H_9I$.—Preparation same as the pre-

¹ *Phil. Mag.*, (4), 9, 214; *Ann. Chem.* (Liebig), 94, 361.

ceding. The residue was crystallized once from a very small amount of absolute alcohol, washed with ether and dried on a porous plate in a vacuum desiccator. These were straw-colored crystals, melting at 98° .

	Calculated.	Found.
Iodine.....	45.79	45.8

Picoline Isobutyl Iodide, $C_6H_5N.C_4H_9I$.—A light yellow sirup, not solidifying at -15° . Prepared by allowing a mixture of the constituents to stand at room temperature for two weeks, also by heating the same mixture for six hours at 100° . If either the mixture or the addition-product is heated much above 100° , decomposition takes place, and on cooling crystals of picoline hydriodide appear. It is very hygroscopic, and no analysis of this compound was made, but these products were used in the preparation of the periodides described later.

Picoline Secondary Butyl Iodide, $C_6H_5N.C_4H_9I$.—This compound was prepared in the same manner as the preceding, but it is much more unstable, and it is doubtful if it was obtained entirely free from hydriodide. When heated, or even if kept on a porous plate in a desiccator, it gradually disappears, breaking up into picoline, hydriodic acid, and (probably) pseudo-butylene. When prepared by allowing the constituents to stand two weeks at room temperature it is a light yellow sirup, which becomes crystalline on cooling to 0° . When prepared by heating the constituents for six hours at 100° , it is obtained as a straw-colored crystalline solid, which could not be dried sufficiently to obtain a melting-point. Both preparations were converted into periodides described later.

	Calculated.	Found.
Iodine.....	45.79	44.64

Picoline and Tertiary Butyl Iodide.—Picoline reacts with tertiary butyl iodide at 100° in the same way that pyridine¹ does; *i. e.*, with formation of the hydriodide, and liberation of isobutylene. The resulting compound melted at 98° , and seemed to be a mixture, so that perhaps a little of the butyl iodide was formed. Analysis showed 51.76 per cent. of iodine.

Picoline and tertiary butyl chloride do not react at the boiling-point of the mixture.

¹ Lippert: *Ann. Chem.* (Liebig), 276, 184.

Picoline Isoamyl Iodide, $C_6H_7N.C_5H_{11}I$.—Amyl iodide (boiling at 148°) was heated with picoline on a sand-bath under reflux condenser. When cold the residue was dissolved in a very small quantity of hot absolute alcohol, placed in a vacuum desiccator and set aside in the cold. Straw-colored cubical crystals formed, which were washed with ether containing a little alcohol, and were dried on a porous plate in a desiccator. It melts at 120° , and turns brown on keeping.

	Calculated.	Found.
Iodine	43.58	43.2

Picoline Allyl Iodide, $C_6H_7N.C_3H_5I$.—This preparation is reported by Ramsay,¹ who states: "All the picoline allyl compounds (of which the iodide, chloride, nitrate, sulphate, and oxalate were made) are sirupy liquids," but this seems to be somewhat inaccurate, in that it does not express all the facts.

Allyl iodide was purified by shaking with dilute potash, drying over calcium chloride, and rectifying. When this is mixed with picoline, the colorless liquid rapidly becomes turbid and yellowish oily drops separate. The reaction proceeds readily at ordinary temperatures, and no heating is necessary. It is complete in about an hour, and a light straw-colored sirup is the resulting product. This rapidly becomes brown on standing, but if cooled to 0° solidifies to a yellowish crystalline mass. Recrystallized from small quantity of hot absolute alcohol it yields cubes, transparent and almost colorless. Melting-point 70° .

	Calculated.	Found.
Iodine	48.603	48.5

Picoline Hydriodide, $C_6H_7N.HI$.—Prepared by conducting dry hydriodic acid gas into picoline kept in a freezing-mixture, and drying on a porous plate over sulphuric acid. A white snowy mass which is rather unstable, and separates readily into its proximate constituents, for which reason the melting-point could not be taken. It was also prepared by adding fuming hydriodic acid (sp. gr. 1.96) to picoline kept in a freezing-mixture, and inducing crystallization by means of the previous preparation. This preparation was attempted by Ramsay,² but he obtained it only in solution.

¹ *Phil. Mag.*, (5), 2, 279.

² *Ibid.*, (5), 2, 271.

	Calculated.	Found.
Iodine.....	57.41	57.62

II. PERIODIDES.

Picoline Hydrogen Diiodide, $C_6H_7N.HI.I$.—Obtained by adding one equivalent of iodine to one of hydriodide, both in alcohol. As the alcohol evaporates, a dark brown oil separates, which on exposure to low temperatures crystallizes in prisms, dark brown, hard and gritty. The melting-point is about 95° but not sharp.

	Calculated for $C_6H_7N.HI.I$.	Found.
Total iodine	72.94	72.5
Additive iodine	36.47	36.25

Crystalline bodies of varying composition were also obtained, giving figures of analysis lower than the above, but no definite formula could be ascribed to them except that they were mixtures of $C_6H_7N.HI.I$ with $C_6H_7N.HI$ in varying proportions.

It is worthy of note that *although the hydriodide is unstable, and the odor of picoline is always noticeable about it, the periodides are quite stable, and no odor is perceptible either of picoline or iodine.* A peculiarity of this and all other perhalides of picoline hydriodide or hydrobromide, is that they all become liquid in contact with water, in which, however, they are almost entirely insoluble. Upon standing in a desiccator at low temperature the liquid will again solidify, the composition and properties being unchanged. This fact was observed by Ramsay in connection with the compound described below, but no explanation is offered to account for it.

Picoline Hydrogen Triiodide, $C_6H_7N.HI.I_2$.—Dark brown octahedral crystals, melting at 44° . It is prepared by adding two equivalents of iodine to one of hydriodide, both in alcohol. After evaporation of the alcohol the oil that remains is exposed to low temperatures when it crystallizes and is dried on a porous plate.

	Calculated for $C_6H_7N.HI.I_2$.	Found.
Total iodine	80.17	79.97
Additive iodine	53.45	53.10

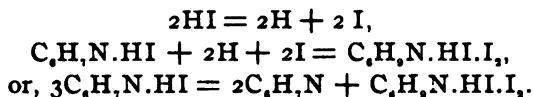
A compound was prepared by Ramsay¹ to which he assigns the same formula. He says "when picoline is mixed with strong

¹ *Phil. Mag.* (5), 2, 273.

aqueous hydriodic acid, and distilled after excess of water has been removed by evaporation, the temperature rises rapidly and the mass turns brown and viscid. If the distillation be continued picoline distils over, and the residue when cool solidifies to a mass of reddish brown needles." These were soluble in alcohol and ether but did not crystallize from them; were insoluble in carbon disulphide and became liquid in contact with water.

	Calculated for		Found.
	$C_6H_7N.HI.I_2$	$C_6H_7N.HI.I_3$	
Total iodine.....	80.17	79.83	80.14
Additive iodine	53.45	53.22

The melting-point is given as 79° , and it is evidently a different compound from that obtained by the writer. It is possible that it is from a different one of the isomeric picolines, but to the writer it appears more probable that the compound obtained by Ramsay is a periodide not of picoline but of a hydropicoline. It is known that the pyridine bases are readily reduced to hydro-compounds, and that hydriodic acid is an active reducing agent at high temperatures. In view of this the following equations would show the probable reactions:



This might be proved or disproved by the preparation of the free base from the periodide, but that compound is obtained in such small quantities as to obstruct such a procedure.

Picoline Hydrogen Pentiodide, $C_6H_7N.HI.I_5$.—A thick greenish black oil obtained by adding picoline hydriodide to the theoretical amount of alcoholic iodine, and allowing the alcohol to evaporate. The oil was washed with dilute arsenite and with water and dried in a desiccator. It did not solidify at -25° .

	Calculated.	Found.
Total iodine	87.08	87.12
Additive iodine	69.66	69.58

α -Picoline Methyl Triiodide, $C_6H_7N.CH_3.I_3$.—Blue-black feathery plates, melting at 134° . This compound, or rather a mixture of its isomers, was prepared by Ramsay¹ by dissolving iodine in an alcoholic solution of the normal iodide. He says

¹ *Phil. Mag.*, (5), 2, 278.

that on cooling it crystallized out in bluish-black feathery plates which transmitted red light, and gives the melting-point as 129° . For the preparation of the α -compound, picoline was fractionated very slowly, carefully, and repeatedly, and the fraction boiling at 131.5° – 132.5° was used. This was converted into the methiodide, which was crystallized once from absolute alcohol. A portion of this was treated with the theoretical amount of iodine in hot alcohol, heated to dissolve the periodide formed and allowed to crystallize. The periodide was then recrystallized once from absolute alcohol, and found to melt at 134° as given above (preparation I). It was also prepared by adding iodopotassium iodide to an aqueous solution of picoline methyl iodide, keeping the latter in excess. By this means an abundant powdery precipitate is formed, which was washed with water, dried and found to melt at 133° (preparation II). Recrystallized from alcohol it was identical with I in appearance and melting-point.

It was obtained once as short brown needles, melting at 135° (preparation III), but on subsequent recrystallization it yielded feathery plates.

	Calculated for $C_6H_7N.CH_3.I_3$, (Ramsay)		I.	Found. II.	III.
Total iodine	77.81	77.59	78.10	77.54	77.62
Additive iodine ..	51.87	52.26	51.50	52.29

β -Picoline Methyl Triiodide, $C_6H_7N.CH_3.I_3$.— β -Picoline was prepared by following the directions of Schwartz¹ in what is usually known as Baeyer's² synthesis. A yield of 15 grams was obtained from 220 grams glycerine, 87.5 grams ammonium phosphate, and 175 grams phosphorus pentoxide. This was distilled and collected in three fractions, and each fraction converted into the methiodide, but as none could be obtained crystalline, they were separately converted into the triiodide by addition of the theoretical amount of alcoholic iodine. A number of products were obtained differing in physical properties (oils, plates, needles, etc.), but all gave figures of analysis agreeing with the formula $C_6H_7N.CH_3.I_3$, and on purification by alcohol and repeated recrystallization were separated into two lots. One of these melted sharply at 134° and agreed in every way with the α -compound described above. The other after several re-

¹ Ber. d. chem. Ges., 24, 1676; Chem. Centrbl., (1891), ii, 172.

² Ber. d. chem. Ges., 2, 398; Chem. Centrbl., (1870), 14.

crystallizations yielded light brown feathery plates, melting at 36° .

These results agree with those of Schwartz, who found that his product contained five per cent. of α -picoline.

	Calculated for $C_6H_7N.CH_2I.I_2$.	Found.	
Total iodine	77.81	78.50	β 77.62
Additive iodine	51.87	51.78	51.73

γ -Picoline Methyl Triiodide, $C_6H_7N.CH_2I.I_2$.— α -Picoline methyl iodide is less soluble in alcohol than its isomers, and the same is true of the corresponding triiodides. A portion of picoline boiling at 137° – 140° (the final fraction from a 400 grams lot) was converted into the methiodide and triiodide, and the latter was crystallized from alcohol. The first crops of crystals were the feathery plates of the α -compound, but finally crystals of another kind were seen, very different in color, shape, and appearance, and easily picked out by hand. These were recrystallized and came out as light brown hexagonal plates which melted at 101° . Repeated recrystallizations from alcohol did not alter the melting-point or crystalline form. The same compound was obtained from other fractions of the picoline, and by exclusion it is reasoned that this must be the γ -compound. On account of the small amount obtained it was not studied as thoroughly as could be desired, but there hardly seems reason to doubt its identity.

	Calculated.	Found.
Total iodine	77.81	78.04
Additive iodine	51.87	51.53

α -Picoline Methyl Pentiodide, $C_6H_7N.CH_2I.I_4$.—Flat needles, blue-black, melting at 60° . It is prepared by adding the corresponding normal iodide to the theoretical amount of alcoholic iodine, or prepared from the triiodide by boiling with the calculated amount of alcoholic iodine. It is also obtained by adding an aqueous solution of the normal iodide to iodopotassium iodide, keeping the latter in excess.

	Calculated.	I.	Found.	II.
Total iodine	85.43	85.7		85.6
Additive iodine	68.34	68.5		68.7

β -Picoline Methyl Pentiodide, $C_6H_7N.CH_2I.I_4$.—A brown-black

oil not solidifying at -25° . Prepared from the corresponding triiodide by boiling with the theoretical amount of alcoholic iodine. The alcohol is then allowed to evaporate, and the oil washed with dilute arsenite and with water, and dried in a desiccator.

	Calculated.	Found.
Total iodine	85.43	85.62
Additive iodine	68.34	68.44

γ -Picoline Methyl Pentiodide, $C_6H_5N.CH_2I_5$.—Slender steel-blue needles, melting at 63° . It is prepared from the corresponding triiodide by boiling with the calculated amount of alcoholic iodine.

	Calculated.	Found.
Total iodine	85.43	85.51
Additive iodine	68.34	68.42

α -Picoline Methyl Heptiodide, $C_6H_5N.CH_2I_7$.—Dark green, feathery plates, melting at 57° . It gives off iodine on exposure to air, and pentiodide remains. Prepared by dissolving the calculated amounts of normal iodide and iodine in hot alcohol, and boiling fifteen minutes under reflux condenser. On cooling an oil separates which soon solidifies, and at the same time crystals are formed.

	Calculated.	Found.
Total iodine	89.146	88.05
Additive iodine	76.411	76.04

γ -Picoline Methyl Heptiodide, $C_6H_5N.CH_2I_7$. Small, flat needles, dark green, melting at 81.5° . It is more stable than the preceding compound. Prepared by treating the corresponding triiodide with the theoretical amount of iodine, and boiling for fifteen minutes under a reflux condenser.

	Calculated.	Found.
Total iodine	89.146	89.14
Additive iodine	76.411	76.11

α -Picoline Ethyl Triiodide, $C_6H_5N.C_2H_5I_3$.—Dark brown oil, obtained by adding two equivalents or less of iodine to one equivalent of the normal iodide, both in alcohol. The oil is separated, washed with dilute arsenite and with water, and dried in desiccator. It remained liquid at -25° .

	Calculated.	Found.
Total iodine	75.70	76.10
Additive iodine	50.47	50.62

α-Picoline Ethyl Pentiodide, $C_6H_7N.C_2H_5.I_5$.—A green-black oil, obtained by adding one equivalent of normal iodide to four of iodine, both in alcohol. It was washed and dried as the preceding. It did not solidify at -25° .

On standing several weeks at 0° and below, a few crystals formed (about 0.1500 gram). These were very long needles, almost black. Dried on porous plate they were found to melt at 80° , and gave figures of analysis under column II below. This is probably the γ -picoline compound.

	Calculated for $C_6H_7N.C_2H_5.I_5$	I.	Found. II.
Total iodine	83.85	83.4	82.9
Additive iodine	67.08	67.1	66.8

Picoline Propyl Triiodide, $C_6H_7N.C_3H_7.I_3$.—Brown oil obtained by adding iodine to normal iodide in theoretical proportions, both in alcohol. It was washed and dried as the preceding. On standing several days at low temperature it crystallized in fine needles, melting at 16° .

	Calculated.	Found.
Total iodine	73.65	73.45
Additive iodine	49.10	49.07

Picoline Propyl Pentiodide, $C_6H_7N.C_3H_7.I_5$.—A green-black oil, obtained by adding normal iodide to alcoholic iodine in proper proportions. It was washed and dried as the preceding. It did not solidify at -25° .

	Calculated.	Found.
Total iodine	82.32	82.1
Additive iodine	65.86	65.7

Picoline Isopropyl Diiodide, $C_6H_7N.C_3H_7.I_2$.—Light brown cubes, melting at 106° . Obtained as the final crop of crystals from the addition of one equivalent of iodine to one of normal iodide. The triiodide is formed at the same time, and in larger quantity, and is separated in crystallization. The diiodide appears to be rather unstable, its alcoholic solution passing to triiodide on warming. The diiodide was also obtained from a portion of normal iodide, containing some alcohol, that had been allowed to stand for about a year, when it was observed that the

sirupy liquid had become brown and crystals had been deposited. These were collected, dried on a porous plate, and recrystallized from alcohol without heating.

	Calculated for $C_8H_7N.C_2H_5.I.I_2$	I.	Found. II.
Total iodine	65.076	65.10	64.82
Additive iodine	32.538	32.61	32.51

Picoline Isopropyl Triiodide, $C_8H_7N.C_3H_7.I.I_2$.—Light brown needles, long and silky, melting at 60° . They are formed when alcoholic iodine is mixed with a solution of normal iodide in any proportion. It is readily prepared free from admixture by mixing in theoretical proportions and allowing to crystallize.

	Calculated for $C_8H_7N.C_3H_7.I.I_2$	I.	Found. II.	III.
Total iodine.....	73.65	72.78	73.74	73.01
Additive iodine.....	49.10	48.66	49.18	48.9

Picoline Isopropyl Pentiodide, $C_8H_7N.C_3H_7.I.I_3$.—Greenish black oil, liquid at -25° . It was obtained by adding normal iodide to the calculated amount of iodine in alcohol, and boiling a few minutes under a reflux condenser. When cold the oil is separated, washed, and dried as in previous preparations.

	Calculated.	Found.
Total iodine	82.33	82.40
Additive iodine	65.86	65.77

Picoline Butyl Triiodide, $C_8H_7N.C_4H_9.I.I_2$.—Light brown needles, long and flat, melting at 33° . They were prepared by adding iodine to the normal iodide in proper proportions, both in alcohol, and allowing to crystallize at low temperature.

	Calculated.	Found.
Total iodine	71.70	71.81
Additive iodine	47.80	47.82

Picoline Butyl Pentiodide, $C_8H_7N.C_4H_9.I.I_3$.—Dark brown oil, not solidifying at -20° . Formed by adding normal iodide to alcoholic iodine in proper proportions.

	Calculated.	Found.
Total iodine	80.856	81.01
Additive iodine	64.685	64.67

Picoline Isobutyl Triiodide, $C_8H_7N.C_4H_9.I.I_2$.—Prepared from the normal iodide in the usual manner. It is a dark brown oil, not solidifying at -15° .

	Calculated	Found.
Total iodine	71.705	71.56
Additive iodine	47.803	48.04

Picoline Isobutyl Pentiodide, $C_6H_7N.C_4H_9.I_5$.—A brown-black oil, not solidifying at -20° . It was prepared from the normal iodide by adding it to alcoholic iodine in proper proportions and boiling under reflux condenser for a few minutes.

	Calculated.	Found.
Total iodine	80.856	80.95
Additive iodine	64.685	64.73

Picoline Secondary Butyl Triiodide, $C_6H_7N.C_4H_9.I_3$.—Brown oil, not solidifying at 0° . It was prepared in the usual manner from the normal iodide previously described. The picoline hydrogen periodide which accompanies it is much more soluble in alcohol, so that as the alcohol evaporates the butyl periodide separates out first, and quite pure. This also applies to the pentiodide described next.

	Calculated for $C_6H_7N.C_4H_9.I_3$.	I.	Found. II.
Total iodine	71.705	71.56	71.63
Additive iodine	47.803	48.04	47.92

Picoline Secondary Butyl Pentiodide, $C_6H_7N.C_4H_9.I_5$.—A green-black oil, not solidifying at 0° . It was obtained in the usual manner from the normal iodide.

	Calculated for $C_6H_7N.C_4H_9.I_5$.	I.	Found. II.
Total iodine	80.856	80.73	81.21
Additive iodine	64.685	64.56	64.77

Picoline Tertiary Butyl Salts are not formed. (See preceding part of this paper under normal iodides.)

Picoline Isoamyl Diiodide, $C_6H_7N.C_5H_{11}.I_2$.—Light brown plates, melting at 96° . They were prepared from the normal iodide previously described by adding alcoholic iodine in theoretical quantity. The triiodide is formed at the same time and crystallizes out first.

	Calculated.	Found.
Total iodine	60.71	60.35
Additive iodine	30.355	30.12

Picoline Isoamyl Triiodide, $C_6H_7N.C_5H_{11}.I_3$.—Light brown, overlapping plates, melting at 22° . They are obtained when-

ever alcoholic iodine is mixed with normal iodide. Prepared pure by mixing in theoretical quantities, and allowing to crystallize at low temperature.

	Calculated.	Found.
Total iodine	69.86	69.5
Additive iodine	46.57	46.3

Picoline Isoamyl Pentiodide, $C_6H_5N.C_5H_{11}I_5$.—Brown-black oil, not solidifying at -25° . It was obtained by mixing alcoholic iodine with normal iodide in theoretical proportions, and boiling a few minutes under reflux condenser.

	Calculated.	Found.
Total iodine	79.44	80.1
Additive iodine	63.55	63.3

Picoline Allyl Triiodide, $C_6H_5N.C_3H_5I_3$.—Purplish brown needles, melting at 62° . Also obtained as light brown feathery plates, of same composition and melting-point, which on recrystallization came out as needles. It is obtained as an oil by adding iodine to the normal iodide in theoretical proportions. On cooling to 0° the oil solidifies, is dried on a porous plate and recrystallized, coming out as above. Ramsay¹ states that no diiodide of the allyliodide was obtained, but goes on to say that by adding iodine to the normal iodide he obtained an oil, insoluble in carbon disulphide, and from which this solvent does not extract iodine. He reports no analysis of it.

	Calculated.	Found.
Total iodine	73.94	73.875
Additive iodine	49.29	49.25

Picoline Allyl Pentiodide, $C_6H_5N.C_3H_5I_5$.—A green-black oil, not solidifying at -25° . It was obtained by adding normal iodide to alcoholic iodine in proper proportions, and heating a short time under reflux condenser.

	Calculated	Found.
Total iodine	82.35	82.25
Additive iodine	65.88	65.76

III. NORMAL CHLORIDES.

Picoline Hydrochloride, $C_6H_5N.HCl.\frac{1}{2}H_2O$.—Prepared by Anderson² in 1846, and again by Ramsay³ in 1876, but no analyses

¹ *Phil. Mag.*, (5), 2, 279.

² *Ibid.*, (4), 9, 145 and 214; *Ann. Chem.* (Liebig), 60, 86.

³ *Phil. Mag.*, (5) 2, 271.

are reported by either. White crystals, extremely deliquescent, very stable, and sublime or distil unchanged except for loss of water. Prepared by acidifying picoline with hydrochloric acid and distilling after excess of water has been expelled; or water can be expelled, and the residue which remains on cooling is dried on porous plates in a vacuum desiccator.

Preparation I was made by acidifying picoline with concentrated hydrochloric acid, evaporating to a thick sirup and allowing to crystallize in desiccator. Crystals were dried on a porous plate in the desiccator, and analyzed. Preparation II is the same, allowed to remain two weeks in the desiccator. Preparation III is the same heated for several hours at 110° , when it was observed that the compound was liquid, and a large part of it had sublimed away. The remainder was cooled in a desiccator and analyzed.

	Calculated for			Found.	
	$C_6H_7N.HCl.\frac{1}{2}H_2O.$	$C_6H_7N.HCl.$	I.	II.	III.
Chlorine ..	25.58	27.36	25.42	25.60	26.81

The melting-point given by Anderson is 160° , but this is only partially verified. Preparation I melted at 165° ; II became liquid at 168° , but did not melt to a clear liquid until a temperature of 198° was reached; III became liquid at 80° and cleared up at 85° . From this it would appear that the melting-point of the *hydrated* salt is about 200° , and of the *anhydrous* about 80° , certainly a very remarkable difference.

α-Picoline Methyl Chloride, $C_6H_7N.CH_2Cl.H_2O$.—Prepared by Ramsay¹ by treating picoline methyl iodide in aqueous solution with freshly precipitated silver chloride. On evaporation to dryness a white, crystalline, deliquescent mass was obtained. No analysis or melting-point was reported. When prepared in this manner, crystallized once from absolute alcohol, and dried on a porous plate in a vacuum desiccator it was found to melt in the neighborhood of 70° , but not sharply, on account of its great hygroscopic power. The crystals contain one molecule of water of crystallization.

	Calculated for		
	$C_6H_7N.CH_2Cl.H_2O.$	$C_6H_7N.CH_2Cl.$	Found.
Chlorine	21.94	23.045	21.72

¹, *Phil. Mag.*, (5), 2, 277.

IV. NORMAL BROMIDES.

Picoline Hydrobromide, $C_6H_7N.HBr$.—Prepared by Ramsay¹ in the same manner as the hydrochloride, and also by brominating picoline and distilling the resulting oil. It was prepared by the writer by conducting dry gaseous hydrobromic acid into picoline, and drying in a desiccator on porous plates. It recrystallized from a very small quantity of absolute alcohol (preparation I) and formed very deliquescent white crystals, melting at 187° (Ramsay). At 306° the compound distils unchanged, coming over as a thick viscid sirup, which on standing in a desiccator gradually solidifies (preparation II).

	Calculated for $C_6H_7N.HBr$.	I.	Found. II.
Bromine	45.94	45.06	46.27

Picoline Methyl Bromide, $C_6H_7N.CH_2Br$.—Prepared by conducting methyl bromide into picoline. Union takes place readily, with evolution of some heat, and the product soon solidifies to a flesh-colored mass. This was dried on porous plates *in vacuo* over sulphuric acid to remove excess of picoline, and recrystallized from a small quantity of absolute alcohol. It forms long colorless needles, which on keeping gradually turn pink. It melts at 217° .

	Calculated.	Found.
Bromine	42.52	42.47

Picoline Ethyl Bromide, $C_6H_7N.C_2H_5Br$.—Prepared by heating the constituents together under a reflux condenser. The formation is not as ready as with the corresponding iodide, but the union is complete in three or four hours. On standing in the cold it gradually solidifies, and is crystallized from a small quantity of absolute alcohol, from which it comes out as transparent colorless crystals. It is somewhat deliquescent and is dried on a porous plate in a desiccator. It melts at 97° .

	Calculated.	Found.
Bromine	39.56	38.9

V. PERBROMIDES.

Picoline Hydrogen Dibromide, $C_6H_7N.HBr.Br$.—Red rhombohedral crystals, melting at 76° . It was prepared by mixing the normal hydrobromide with the corresponding tribromide in equi-

¹ *Phil. Mag.*, (5), 2, 271.

molecular proportions, in presence of a small amount of absolute alcohol. On standing the dibromide crystallizes out and is dried on porous plates.

	Calculated.	Found.
Total bromine	62.95	62.2
Additive bromine.....	31.47	31.1

Picoline Hydrogen Tribromide, $C_6H_7N.HBr.Br_2$.—Transparent oil, deep red in color, not solidifying at -15° . It was prepared by adding bromine to an aqueous solution of the hydrobromide, or by aspirating vapors of bromine through the same.

	Calculated for $C_6H_7N.HBr.Br_2$.	Ramsay's analyses.		Found.
Total bromine.....	72.00	71.17	68.04	72.74
Additive bromine.....	48.00	48.21

Ramsay¹ describes a compound to which he assigns the same formula, and which he obtained by heating the constituents in a sealed tube to 190° , and also by adding bromine to a solution of the hydrobromide. His compound crystallized from hot water in yellow crystals, melting at 85° with loss of bromine. The second method could not be verified, and the first was not tried by the writer. Picoline hydrogen tribromide should melt lower than the corresponding triiodide (44°); and if a solid, should be liquefied by water. In view of these and other facts it appears that Ramsay must have had quite a different compound, perhaps $C_6H_5BrN.HBr.Br_2$, which although differing in empirical formula by only one hydrogen atom would have properties very different from the compound obtained by the writer.

α -Picoline Methyl Tribromide, $C_6H_7N.CH_3Br.Br_2$.—When vapors of bromine are aspirated through an aqueous solution of picoline methyl bromide to saturation, a red oil is precipitated, which soon solidifies. On recrystallizing from alcohol it comes out as orange-yellow plates, melting at 111° , and having a faint odor of bromine.

	Calculated for $C_6H_7N.CH_3Br.Br_2$.	I.	II.
Total bromine	68.94	67.99	69.21
Additive bromine	45.96	45.50	45.42

Picoline Ethyl Tribromide, $C_6H_7N.C_2H_5Br.Br_2$.—On aspirating vapors of bromine through an aqueous solution of picoline ethyl

¹ *Phil. Mag.*, (5), 2, 275.

bromide, a transparent deep red oil separates as before, but in this case it remains liquid in a freezing-mixture.

	Calculated.	Found.
Total bromine	66.26	66.34
Additive bromine.....	44.17	44.22

VI. IODOBROMIDES.

Picoline Hydriodide Bromide, $C_6H_7N.HI.Br$.—Dark red crystals, melting at 68° . Prepared by mixing equimolecular portions of picoline hydriodide and picoline hydriodide dibromide ; or of picoline hydrogen diiodide with the corresponding dibromide, in presence of a small quantity of absolute alcohol.

	Calculated for $C_6H_7N.HI.Br$.	Found.
Total halogens.....	68.726	68.57
Total iodine	42.156	41.93
Total bromine	26.570	26.64
Additive halogen (bromine).....	26.570	26.72

Picoline Hydriodide Dibromide, $C_6H_7N.HI.Br_2$.—Dark red crystals melting at 58° . It was obtained in a number of ways. I. Two molecular portions, of tribromide and one of triiodide were mixed in presence of a small quantity of absolute alcohol. II. Picoline is diluted with water and acidified with hydrobromic acid, potassium iodide is added and vapors of bromine are aspirated through to saturation. By this means a red oil is obtained which solidifies to a crystalline mass, and melts at 57° . III. Vapors of bromine were aspirated through water in which was suspended picoline hydrogen diiodide. Red crystals were obtained, melting at 48° .

	Calculated for $C_6H_7N.HI.Br_2$.	I.	Found. II.	III.
Total halogens	75.295	74.08	75.47	73.45
" iodine.....	33.31	29.09	29.63	21.99
" bromine.....	41.985	44.82	45.50	51.29
Additive halogen.....	41.985	42.15	41.94	42.21
Atomic ratio, I : Br	1 : 2	1 : 2.4	1 : 2.4	1 : 3.7

α -Picoline Methyl Iodide Dibromide, $C_6H_7N.CH_3I.Br_2$.—When vapors of bromine are aspirated through an aqueous solution of picoline methyl iodide (or any normal iodide), the first thing noticed is a brownish precipitate, evidently a triiodide, resulting from the displaced iodine which *immediately* combines with the

normal iodide still in excess. As the process is continued the precipitate becomes lighter in color (due to its conversion into iodobromide), and the supernatant liquid becomes clear. A portion of the precipitate was removed at this point and recrystallized from alcohol (I), and the remainder further treated with bromine for a considerable time and then recrystallized (II). I melted at 121° , and II at 110° .

That the triiodide is converted into iodobromide was shown by suspending it in water and aspirating vapors of bromine through it for some time. The product was then crystallized from alcohol and yielded fine orange-red needles, melting at 121° (III).

Prepared purest and best by mixing two molecular portions of tribromide with one of triiodide, and crystallizing from alcohol. Slender orange-red needles formed, two to three inches long, melting at 121.5° (IV).

	Calculated for $C_6H_7NCH_2I.Br_2$	I.	Found.	III.	IV.
Total halogens.....	72.630	71.46	70.35	70.21	71.83
" iodine	32.136	27.36	18.02	16.30	31.70
" bromine	40.494	43.90	51.71	53.91	40.28
Additive halogen ...	40.494	40.87	40.53	40.50	40.48
Atomic ratio I:Br ..	1:2	1:2.2	1:4.5	1:5.2	1:2

The compound is perfectly stable and does not decompose at 220° , although a faint odor of bromine is usually noticeable in the bottle.

On gently warming a solution of potassium iodide, in which is suspended any one of the above preparations, the orange-red color immediately disappears, and the crystals become brown. Recrystallized from alcohol they then melt at 133° .

	Calculated for $C_6H_7N.CH_2.I.I_2$	Found.
Total iodine	77.81	77.63
Additive iodine	51.87	51.20

α -Picoline Methyl Iodide Iodobromide, $C_6H_7N.CH_2.I.Br$.—Long, flat, interlaced needles, reddish brown in color, melting at 113° . It was prepared by mixing two molecular portions of α - $C_6H_7N.CH_2.I.I_2$, with one of α - $C_6H_7N.CH_2.Br.Br$, and crystallizing from hot alcohol.

	Calculated for $C_6H_7N.C_2H_5I.Br.$	Found.
Total halogen	75.525	75.53
" bromine	18.097	18.15
" iodine	57.428	57.24
Atomic ratio I : Br	2 : 1	2 : 1

Picoline Allyl Iodide Dibromide, $C_6H_7N.C_3H_5I.Br_2$.—Orange-yellow plates, melting at 84° , perfectly stable and odorless. It was prepared by aspirating bromine through an aqueous solution of the normal iodide, and crystallizing from alcohol. The allyl group does not become saturated by the bromine.

	Calculated for $C_6H_7N.C_3H_5I.Br_2$	Found.
Total halogen	68.13	68.27
" bromine	37.99	38.15
" iodine	30.14	29.93

VII. AMINE PERHALIDES.

Picoline Dibromide, $C_6H_7N.Br_2$.—These compounds were prepared by Ramsay,¹ and are given here for the sake of completeness. The dibromide is formed by addition of bromine to picoline in chloroform, and evaporating the chloroform in a vacuum desiccator. Small interlaced needles formed which lose bromine on standing.

Picoline Iodochloride, $C_6H_7N.ICl$.—Prepared by Ramsay¹ in the same manner as the preceding by adding iodine chloride to picoline in chloroform. Long yellow needles formed.

Picoline Periodide, $C_6H_7N.I_2$.—The existence of compounds analogous to pyridine tetriodide is indicated, although they were not obtained by the writer in a pure form. It is well known that a solution of iodine in chloroform is violet. If now a drop of picoline be added, the color at once changes to brown. On allowing the chloroform to evaporate, a thick sirup remained, but crystals were not obtained.

DISCUSSION.

The compounds described in the preceding pages are in every way analogous to those of pyridine, and with few exceptions agree with generalizations based upon a study of the pyridine compounds.²

¹ *Phil. Mag.*, (5), 2, 275.

² Prescott : Pyridine Alkyl Iodides, *This Journal*, 18, 91.

In each case where a melting-point could be taken, the normal iodides of picoline were found to melt higher than the corresponding pyridine compound, and the same is generally but not invariably true of the periodides. Also, the addition-products with methyl bromide follow the rule, but the reverse is true with ethyl bromide; while the other normal bromides and chlorides do not give melting-points sufficiently sharp for comparison. The relation existing between the boiling-points of the alkyl iodides and the melting-points of their pyridine addition-products is found to hold true with picoline in all cases except the isopropyl, amyl, and various butyl compounds, in which cases the melting-points are more or less anomalous.

The generalizations of Carnally¹ in regard to isomeric compounds were found to apply in nearly all instances. These are: "Of two isomers, that is most soluble which has the lower melting-point." "Of two or more isomeric compounds, those whose atoms are the most symmetrically or compactly arranged, melt higher than those in which the arrangement is asymmetric or in long chains." "Those compounds melt highest which have the greatest number of side chains; and compactness sometimes overbalances increase in atomic weight." Exceptions to these are observed in the case of the butyl and isobutyl compounds, both normal and superiodides. Also, compounds of γ -picoline should melt highest of the three isomers, but this is not the case with the methyl triiodides, and probably not with the normal methiodide.

From a practical or analytical point of view, perhaps the most important result of this research is the separation or the identification of the three isomeric picolines by means of their methyl triiodides. The separation has not been studied in all its aspects and possibilities on account of the scarcity of material and difficulty of preparation of the β - and γ -picolines. The picoline drawn upon for the preceding preparations was a Kahlbaum article, boiling at 130° – 134° . It consisted very largely of α -picoline, but contained some pyridine and some γ -picoline. The larger part distilled over between 131° and 133° , but on slow and careful fractionation a small amount (six grams from a 400 grams

¹ *Phil. Mag.*, (5), 13, 116 and 180; *J. Chem. Soc.*, 53, 78a.

lot) was obtained which boiled at 137° – 140° , and yielded the γ -picoline compounds previously described.

At present there is no ready method of obtaining the tertiary base in this series after it has once combined with an alkyl iodide to form a salt of the quaternary base, for on distilling the hydroxide of the quaternary base decomposition takes place, the ring is broken down and an aliphatic amine is produced, along with other products of decomposition, and no odor of picoline could be detected in the distillate. The use of the method as a *separation* is therefore diminished, but it is promising as a means of identification of the picolines.

In regard to the conditions of formation of the various periodides, it appears that the lower periodides (usually a triiodide) are formed whenever iodine is added to a normal iodide, or when the iodine is not in excess; and that the pentiodides are formed whenever these conditions are reversed. For formation of the heptiodides it is necessary to boil for some time with a considerable excess of iodine. The heptiodides are unstable, giving off iodine on standing and becoming pentiodides. The diiodides are also unstable (except $C_6H_5N.HI.I$) as on boiling their alcoholic solutions they change to triiodides and normal iodides.

In solution the additive halogens are very reactive, and rearrange themselves with the greatest readiness. Lower periodides take up more iodine and change to pent- and heptiodides on boiling with alcoholic iodine; and these can be changed to triiodides with equal readiness by boiling with normal iodide. This readiness of rearrangement is most noticeable in the case of the complex perhalides, and was studied thoroughly in connection with the picoline methyl- and allyl-iodobromides.

The study of the complex perhalides, those with more than one halogen element, is of interest as bearing upon questions of constitution and the structural character of the halogens. When solutions of a periodide and a perbromide are mixed, or when a mixture of the two is dissolved in alcohol, reaction appears to be instantaneous, and an iodobromide results. The iodobromides are isomorphous with the perbromides, and if the latter be in excess it will crystallize out with the iodobromide in homogeneous crystals, so that different products may vary widely in composition, and yet be identical in appearance and even in

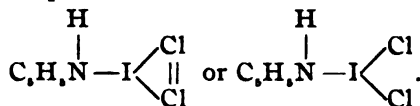
melting-point. The same results are obtained when bromine is aspirated through a solution of normal iodide or through a suspension of a periodide. At one time the question was raised in this research whether the complex perhalides were not in reality *mixtures* of the *simple* perhalides, but this now appears to be improbable. In view of these conclusions it will be seen that isomerism in the arrangement of the halogens is impossible, and that of the two formulas $C_6H_7N.CH_2I.Br$, and $C_6H_7N.CH_2Br.IBr$ only one can exist, and only one such compound is known.

The proof of the structure of the complex perhalides is perhaps not complete, but from a careful consideration of the facts at hand, the writer takes the view that *in every case it is the halogen of higher atomic weight that is next to the nitrogen*. The facts bearing on this question are as follows :

1. The great ease of formation and stability¹ of the periodides, and the power of iodine to hold a large number of additive atoms of iodine.²
2. The non-existence³ of perchlorides.
3. The intermediate position of perbromides; the limit of the number of additive atoms being usually two, but in some cases four⁴ atoms of bromine.⁴
4. Iodobromides are more stable than perbromides.
5. Iodine displaces bromine or chlorine completely, and bromine displaces chlorine completely,⁵ a reversal of the usual reactions of these elements ; while bromine or chlorine displaces *all but one* of the iodine atoms in the molecule, and chlorine displaces *all but one* of the bromine atoms.

Since no perchlorides are formed, chlorine cannot hold chlo-

rine, and the formula $C_6H_7N : Cl \begin{array}{c} \diagup I \\ || \\ \diagdown Cl \end{array}$ is untenable, and the compound of that composition would have the constitution



¹ See under Picoline Hydrogen Diiodide, in previous part of this paper.

² Atropine Enneaiodide, $C_{17}H_{23}NO_8.HI.I_9$, Prescott and Gordin: This Journal, 20, 711.

³ Trowbridge and Diehl: This Journal, 19, 571.

⁴ Quinoline Hydrogen Pentabromide, $C_9H_7N.HBr.Br_4$, Trowbridge: This Journal, 21, 68.

⁵ Trowbridge and Diehl: This Journal, 20, 563.

The general properties of these periodides and perhalides are much the same as those of the corresponding pyridine compounds. All the pentiodides, except two of the picoline methyl pentiodides are oils, while the triiodides with few exceptions are nicely crystalline. They are all insoluble in water, but are soluble in alcohol or chloroform. They are soluble in hot solutions of alkali carbonates without color (formation of iodate and iodide), and from such solution they are reformed and precipitated by addition of acids. They are soluble in caustic alkalies with more or less decomposition; and on boiling with alkalies iodoform appears to be formed. Normal halides of the tertiary base (picoline hydrochloride) are decomposed by solutions of alkali bicarbonates, yielding the free base. Solutions of potassium iodide convert all perhalides to pure periodides. The perhalides of the quarternary base are in general very stable, and some of the liquid periodides may be boiled for hours with decinormal arsenite before solution takes place.

METHODS OF ANALYSIS.

In analyzing the compounds described, volumetric processes were used almost exclusively, although the results were checked frequently by gravimetric estimations.

I. ANALYSIS OF COMPOUNDS CONTAINING ONLY ONE HALOGEN.

For estimating halogens in the normal halides, the Volhard method was used, precipitating with decinormal silver nitrate and retitrating with thiocyanate. The volumetric silver solution was standardized and tested at intervals by precipitating a definite portion and weighing the silver chloride formed.

In perhalides containing only one halogen, the additive or exterior halogen, was estimated with decinormal arsenious acid in sodium bicarbonate, retitrating with iodine. The arsenite was made by weighing resublimed arsenic, dissolving in sodium bicarbonate and when cold diluting to required volume. Arsenite has this advantage over thiosulphate, that both the arsenate and arsenite of silver are soluble in nitric acid, so that there are no products of reaction to interfere with the estimation by the Volhard method of the total halogen present in the same solution. When thiosulphate is used there are products which do interfere.

For estimating the total halogen, the easiest and most rapid method is to dissolve the perhalide in alkaline arsenite, with or without the aid of alcohol, precipitate with decinormal silver nitrate, and titrate the excess of silver with thiocyanate. This was compared with the zinc dust reduction and found to give identical results, with the advantage that no filtering is necessary.

The method of analysis for both additive and total halogen in a simple periodide or perbromide is as follows: A weighed portion is covered with about 10 cc. of alcohol, and decinormal arsenite is added till the perhalide is dissolved and the color destroyed, and the excess of arsenic is titrated with iodine in the ordinary way using starch paste as an indicator. The difference, multiplied by the decinormal factor of the halogen gives the weight of *additive halogen* present in the original sample.

After the titration with iodine, the total halogen can be estimated in the same portion, provided it is known how much iodine was added in the first titration. For this purpose a convenient solution is made by dissolving 12.685 grams iodine and 24.8925 grams potassium iodide in a small amount of water, and diluting to one liter. One cc. of this solution, reduced with arsenic, is equal to two and five-tenths cc. of decinormal silver nitrate, or in other words the solution is decinormal to arsenic and fourth-normal to silver.

II. ANALYSIS OF MIXTURES OF TWO HALOGEN ELEMENTS.

When two halogens are present, their separate estimation is not quite so easy, but may be accomplished in the following manner: A weighed portion of the complex perhalide is reduced with zinc dust or arsenic as preferred, or any compound containing two halogens, is converted to the condition of a soluble iodide, etc. The halides in the clear solution or filtrate are precipitated with a known amount of standard silver nitrate, the precipitate is collected in the usual manner and weighed, and the filtrate containing the excess of silver is titrated with thiocyanate. By means of the following formulas the percentages are calculated.

Given :

a = weight of substance taken for analysis.

b = weight of silver halides obtained.

c = no. of cc. of $\frac{N}{10}$ silver nitrate required.

To find :

p = percentage of total halogen.

r = atomic ratio of halogens.

p' = percentage of one halogen.

$p'' = p - p'$ = percentage of the other halogen.

For iodine and bromine the formulas are :

$$p = \frac{100b - 1.0792c}{a} \quad [1]$$

$$r = \frac{0.023477c - b}{b - 0.018787c} = \frac{\text{atoms of bromine}}{\text{atoms of iodine}} \quad [2]$$

$$p' = \frac{126.85(b - 0.018787c)}{0.469a} = \text{per cent. iodine} \quad [3]$$

$$p'' = \frac{79.95(0.023477c - b)}{0.469a} = \text{per cent. bromine} \quad [4]$$

For iodine and chlorine they are :

$$r = \frac{0.023477c - b}{b - 0.014337c} = \frac{\text{atoms of chlorine}}{\text{atoms of iodine}} \quad [2a]$$

$$p' = \frac{126.85(b - 0.014337c)}{0.914a} = \text{per cent. iodine} \quad [3a]$$

$$p'' = \frac{35.45(0.023477c - b)}{0.914a} = \text{per cent. chlorine} \quad [4a]$$

For bromine and chlorine they become :

$$r = \frac{0.018787c - b}{b - 0.014337c} = \frac{\text{atoms of chlorine}}{\text{atoms of iodine}} \quad [2b]$$

$$p' = \frac{79.95(b - 0.014337c)}{0.445a} = \text{per cent. bromine} \quad [3b]$$

$$p'' = \frac{35.45(0.018787c - b)}{0.445a} = \text{per cent. chlorine} \quad [4b]$$

The deduction of the formulas for iodine and bromine is as follows :

Let m = weight of silver in b
 n = weight of halogen in b

$$m + n = b$$

$$m = 0.010792 c$$

$$n = b - m = b - 0.010792 c$$

but $a : n :: 100 : p$

$$\text{or } p = \frac{100 n}{a} = \frac{100 b - 1.0792 c}{a} \quad [1]$$

Also let w = combining weight of mixed halogens.

x = number of atoms of iodine in one molecule of a .

y = " " " " bromine in one " " a

$r = \frac{y}{x}$ = atomic ratio of bromine to iodine.

$$\text{then } w = \frac{126.85 x + 79.95 y}{x + y} = \frac{126.85 + 79.95 r}{1 + r}$$

$$r = \frac{126.85 - w}{w - 79.95}$$

but $m : n :: 107.92 : w$

$$\text{or } w = \frac{107.92 n}{m} = \frac{107.92 (b - 0.010792 c)}{0.010792 c}$$

$$w = \frac{10000 (b - 0.010792 c)}{c} = \frac{10000 b}{c} - 107.92$$

$$r = \frac{234.77 - 10000 b}{10000 b - 187.87 c} = \frac{0.023477 c - b}{b - 0.018787 c} \quad [2]$$

Also:

$$0.010792 \left(\frac{1}{1 + r} \right) c = \text{weight of silver combined with iodine in } b$$

$$0.010792 \left(\frac{r}{1 + r} \right) c = \text{ " " " " " bromine " } b$$

$$\text{then } \frac{0.012685 c}{1 + r} = \text{ " " iodine in } b \text{ or in } a$$

$$\frac{0.007995cr}{1+r} = \text{weight of bromine in } b \text{ or in } a$$

$$p' = \frac{100}{a} \times \frac{0.012685c}{1+r} = \frac{126.85(b - 0.018787c)}{0.469a} \quad [3]$$

$$p'' = \frac{100}{a} \times \frac{0.007995cr}{1+r} = \frac{79.95(0.023477c - b)}{0.469a} \quad [4]$$

In conclusion profound thanks are expressed to Prof. A. B. Prescott, in whose laboratory and under whose supervision the work has been done.

CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN,
ANN ARBOR, June 9, 1899.

THE DETERMINATION OF NICKEL IN NICKEL-STEEL.

BY GEO. WM. SARGENT.

Received July 17, 1899.

THE results obtained in this laboratory by the following method have been such as to warrant my placing it before fellow-chemists, who, I believe, will find the method more reliable and more pleasant to work than most procedures now in vogue for the determination of nickel in steel.

The method in detail is as follows: Dissolve two grams of the steel in hydrochloric acid (1.1 sp. gr.), add one cc. of strong nitric acid to oxidize the iron, and evaporate to hard dryness. Take up the residue in twenty cc. hydrochloric acid (1.1 sp. gr.), evaporate to ten cc. volume, and transfer the solution to a 250 cc. separatory funnel.¹ Use warm hydrochloric acid (1.1 sp. gr.) for washing the contents of the beaker into the funnel, taking care to keep the volume as small as possible. Cool the funnel and its contents under the spigot, then introduce forty cc. of ether free from alcohol, which has just been thoroughly shaken with five cc. of strong hydrochloric acid, and shake vigorously for ten minutes, keeping the temperature from rising by frequently holding the funnel under the running water. Allow the funnel to stand a few minutes, draw off the lower aqueous layer containing the nickel, copper, manganese, and other chlorides not held by the ether, wash down the sides of the separatory funnel with hydrochloric acid (1.1 sp. gr.), shake with the

¹ See method of Chase for the "Determination of Nickel and Aluminium in Steel" in the appendix of "The Chemical Analysis of Iron," by Blair, third edition.

ether, and run the washings into the beaker with the chlorides of nickel, copper, etc. Two washings with five to ten cc. of hydrochloric acid are sufficient to completely remove the nickel and other chlorides from the funnel. The ethereal solution containing the ferric chloride is run into a residue bottle and later the ether recovered by distillation. Boil the liquid containing the nickel to completely expel the ether and add to the boiling solution, diluted to at least 200 cc. an excess of ammonia and ten to twenty drops of bromine water, to precipitate any iron or manganese. Filter, wash, redissolve in hydrochloric acid, reprecipitate with ammonia and bromine water, and filter. Combine the filtrates, boil, remove any precipitate, acidulate with hydrochloric acid, boil until the excess of bromine has been expelled, and precipitate the copper as sulphide. The filtrate from the copper sulphide which contains nickel only, is evaporated to a volume of 100 cc., cooled and one cc. excess of ammonia added. Now introduce into the nickel solution, which is best contained in an Erlenmeyer flask, five cc. of silver nitrate (one-half gram silver nitrate in a liter of water), and the same amount of a two per cent. solution of potassium iodide. Run into the opalescent solution, which should have a temperature slightly lower than that of the hand, standard potassium cyanide (one cc. equal to about 0.001 gram of nickel) until the liquid becomes clear and bright. This titration is best made with a black background, when the end-reaction becomes very sharp and decided after a little practice, half a drop only being sufficient to discharge the opalescence.¹

The potassium cyanide solution is standardized by introducing into an Erlenmeyer flask ten cc. of a solution containing a known amount of recrystallized nickel nitrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ten cc. of hydrochloric acid (1.1 sp. gr.), one cc. excess of ammonia, five cc. each of the silver nitrate and potassium iodide, diluting the whole to 100 cc., and running in the potassium cyanide until the solution clears. It is necessary that a blank be made upon the silver nitrate and potassium iodide used as the indicator, under the same conditions as the standardization, and this amount deducted from each titration.

¹ See "Determination of Nickel in Nickel-Steel," by E. D. Campbell and W. H. Andrews: *This Journal*, 17, 127.

The presence of varying quantities of ammonium chloride in the nickel solution to be titrated has no effect on the titration. This is evident from the following :

Taken.			Found.				
NH ₄ Cl present. Grams.	Ni(NO ₃) ₂ . cc.	Weight of Ni. Gram.	Readings.		Difference.	Blank.	Weight of Ni. Gram.
			First.	Second.			
1	20	0.02	0.0	20.2	20.2	0.45	0.01996
3	20	0.02	20.2	40.5	20.3	0.45	0.02007
7	20	0.02	0.0	20.2	20.2	0.45	0.01996

1 cc. potassium cyanide solution = 0.001011 gram nickel.

Some of the results obtained by the foregoing method I append :

Mark.	Solution of KCN equivalent to Ni. cc.	Weight of nickel found. Gram.	Nickel. Per cent.
389	27.65	0.02795	1.397
389	27.65	0.02795	1.397
389	27.55	0.02785	1.392
390	28.60	0.02891	1.445
390	28.55	0.02886	1.443
382	30.40	0.03073	1.536
382	30.20	0.03053	1.527
387	31.00	0.03134	1.567
387	30.70	0.03104	1.552
387	31.00	0.03134	1.567
109	51.00	0.05156	2.578
109	51.30	0.05190	2.595

1 cc. potassium cyanide = 0.001011 gram nickel.

The above determinations were made on steels in which the manganese did not exceed one-tenth per cent. and in which there was no copper.

Different amounts of nickel were mixed with solutions containing two grams of iron and the nickel determined therein :

Taken.		Found.	
Ni(NO ₃) ₂ solution. cc.	Weight of nickel. Gram.	KCN solution equivalent to Ni. cc.	Weight of nickel. Gram.
30	0.03	29.60	0.02992
30	0.03	29.05	0.02937
40	0.04	39.60	0.04003
40	0.04	39.70	0.0401
45	0.045	44.05	0.0445

For the estimation of nickel in ferronickel, dissolve twenty grams of the sample in aqua regia, evaporate to hard dryness take up with hydrochloric acid (1.1 sp. gr.), transfer to a liter flask, and dilute to the mark with water. Remove fifty cc., to which add five cc. strong hydrochloric acid, and concentrate to one-sixth its volume. Transfer to the separatory funnel, and proceed as with the steel.

A sample of ferronickel which, by an unknown method contained 33.93 per cent. of nickel, yielded 33.80, 34.00, 33.88, and 33.96 per cent. Another sample which, according to one chemist, contained 34.95 per cent. of nickel, gave 35.15 and 35.26 per cent.

The above-described method is, as can readily be seen, a combination of a modified portion of the method of Chase, with a slightly changed part of the procedure given by Campbell and Andrews. In the course pursued by Chase, two ether separations are necessary to remove the ferric chloride, while the separation, as worked by us, need not be repeated; but little ferric chloride is left, and the two ammonia precipitations are sufficient to completely remove the iron from the nickel.

With regard to the titration with potassium cyanide, that may be accomplished in the presence of most all the salts of ammonium and the mixed alkalies except the nitrates. The excess of ammonia should not in any case exceed three cc.¹

While in steels, about which one knows nothing, it will be necessary to hunt for copper, yet in the general run of furnace work, copper is absent, and knowing such to be the case, the working with the unpleasant gas, hydrogen sulphide, is done away with entirely. As far as time is concerned, the method is short, requiring no longer time than the method of Chase.

In conclusion, I wish to here acknowledge the assistance of Mr. Clarence Ebaugh and Mr. John K. Faust in working out this method.

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¹ See "Estimation of Cyanogen," by Wm. J. Sharwood: This Journal, 19, 415.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 41.]

THE QUANTITATIVE ESTIMATION OF BORIC ACID IN TOURMALINE.¹

BY GEORGE W. SARGENT.

Received July 21, 1899.

INTRODUCTION.

NOTHING of the constitution of this mineral is understood. In fact, exceedingly little is known concerning the structure of much less complex minerals. Structural formulas have been proposed, but these are conjectures only.

The problem that confronts the chemist undertaking to throw light upon the constitution of any of the products of nature's laboratory, is a very difficult one. No mode of attacking the problem has ever been devised. Substitutions, syntheses, and decompositions cannot be made as with organic bodies. There is no means of estimating the size of the molecule. The question of determining which elements are linked together in many instances seem unanswerable. Again, many elements are capable of existing in two conditions; this complicates the problem still further. Before attempting to answer these questions, however, the composition of the body must be known.

In a careful review of the literature of mineralogy, it will be noticed that in many cases some constituent of a mineral has been determined by difference, owing probably to the fact that no good direct method of estimating it existed at that time. Every chemist feels the necessity of directly determining any constituent. It is especially desirable that this be done in the analyses of complex substances. It may happen that many years have elapsed since the analysis of the mineral was made. Since then the old methods probably have been shown to be inaccurate, hence a redetermination is desirable. Owing to the difficulty of estimating boric acid, Rammelsberg, in numerous instances, in his analyses of tourmaline, obtained it by difference.

Boric acid constitutes from six per cent. to twelve per cent. of this mineral. Silica and alumina are its common associates from which it is separated with great difficulty. Since the time

¹ From the author's thesis presented for the Ph.D. degree, 1898.

of Rammelsberg, many methods have appeared, but few have been found applicable to insoluble borates or borosilicates; with tourmaline, they have proved tedious or unreliable. A chronological review of the various methods for the determination of this acid may be interesting. At least, it will show the condition in which the quantitative determination of boric acid rests at the present time.

HISTORICAL RÉSUMÉ.

Probably the first work that was done toward the quantitative determination of boric acid, was that of Arfvedson.¹ By heating a mixture of borax and calcium fluoride with sulphuric acid, he volatilized the boron as fluoride; the sodium sulphate resulting from this treatment was dissolved out with water, evaporated to dryness, weighed, and the boric acid calculated.

Berzelius² attempted the determination by precipitating boron as potassium borofluoride. Berzelius also used Arfvedson's method with success, but in place of the calcium fluoride and sulphuric acid, he took hydrofluoric and sulphuric acids. In 1828, Menil³ endeavored to estimate boric acid by means of the silversalt, $3\text{Ag}_2\text{O} \cdot \text{B}_2\text{O}_3$, but met with little success. Gay Lussac,⁴ in the year 1830, called attention to the titration of borax by a sulphuric acid solution with tincture of litmus as the indicator. The reaction is: $\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{B}_2\text{O}_3$. The liquid changes color only when free sulphuric acid is present. This was the first volumetric method proposed.

Rose⁵ was the first to volatilize boric acid as the ethyl ester and obtain its amount by difference. This was in 1850, but as early as 1732, Claude Geoffrey knew that boric acid imparted a characteristic green color to the alcohol flame and in 1818, Stromeyer⁶ mentioned the volatility in an alcoholic solution and the characteristic green color given to the burning liquid. Rose, in his paper, gave a second method, in which a weighed amount of sodium carbonate was added to the borate, evaporated to dryness, and ignited until there was no further evolution of carbon

¹ *K. Velensk. Acad. Handb.*, (1822), 22, and *Schweigg. Jour.*, 8, 7.

² *Lehrbuch*, 3, Aufl. 84; *Pogg. Ann.*, (1824), 2, 118.

³ *Jsb. d. Chem. und Phys.*, 2, 364.

⁴ *Ann. Chem. et Phys.*, 40, 398.

⁵ *Pogg. Ann.*, 80, 261.

⁶ *Ibid.*, 61, 179.

dioxide. The residue of sodium carbonate and boron trioxide was weighed and from this the boric acid calculated.

Berzelius' method gave poor results, owing to the solubility of the precipitate of potassium borofluoride in alcohol, with which it was washed to free it from potassium fluoride. Weber¹ tried modifying the method of Berzelius, in order to avoid the formation of the large quantity of fluoride, but did not succeed. Rammelsberg² found that if the alcohol used for washing the precipitate was free from water, potassium fluoride contaminated the precipitate, and that alcohol containing water dissolved some of the potassium borofluoride. Schweitzer³ estimated the base and determined the boric acid by difference, by evaporating the base with hydrochloric acid until all the acid was expelled and estimating the chlorine as silver chloride.

In 1856, Kraut⁴ showed that a borax solution boiled with ammonium chloride, reacted according to the following equation: $\text{Na}_2\text{B}_4\text{O}_7 + 2\text{NH}_4\text{Cl} = 2\text{NaCl} + 2\text{B}_2\text{O}_3 + 2\text{NH}_3$, and the ammonia could be caught in a standard acid solution, and thus the boric acid determined. This same year, the method of Stromeyer⁵ appeared. He added to the solution of the borate two equivalents of potassium hydroxide to one equivalent of boron trioxide contained in the borate, then an excess of hydrofluoric acid and evaporated to dryness. The residue he dissolved in a twenty per cent. solution of potassium acetate, and filtered through a weighed filter, using a gutta percha funnel. The precipitate was washed first with a solution of potassium acetate to remove potassium fluoride, then with alcohol, dried at 100° C., and weighed. Upon applying this method to a silicate, Stromeyer obtained 97.5 per cent. of all the boron trioxide.

Where the boric acid content was approximately known, Schaffgotsch⁶ added to the solution a weighed amount of sodium carbonate, in which not less than one and not more than two equivalents of sodium oxide (Na_2O) to two equivalents of boron trioxide were contained. After evaporation to dryness

¹ *Pogg. Ann.*, 80, 276 (1850).

² *Ibid.*, 80, 466 (1850).

³ *Pharm. Centrbl.*, Nr. 24, 390, and Fresenius' *Anleitung zur quant. Analyse*, 6 Aufl., (1875), 1, 424.

⁴ *Henneberg's Jour. für Landwirtsch.*, 4, 112; abs. by *Ztschr. anal. Chem.*, (1863), 73.

⁵ *Ann. Chem. (Liebig)*, 100, 82.

⁶ *Pogg. Ann.*, (1859), 107, 427.

and ignition, the residue was sodium oxide and boron trioxide, the weight of which, less the weight of the sodium oxide taken, gave the boron trioxide. This method is essentially the same as that of Rose.

Marignac¹ in a solution containing alkali salts only, estimated the boric acid thus: After the addition of magnesium chloride, ammonium chloride, and ammonia, he evaporated the solution to dryness in a platinum dish. The residue after ignition was taken up with water and the insoluble portion removed: the filtrate was made ammoniacal, evaporated to dryness, ignited, the residue taken up with water, and the insoluble portion filtered off as before. This was repeated three times. The insoluble portions were ignited and weighed as magnesium pyroborate; the magnesia was determined by dissolving the pyroborate in nitric acid and precipitating as magnesium ammonium phosphate, and from this the boric acid was obtained by difference. Insoluble borates were fused with sodium carbonate, the melt extracted with water, and the solution acidified with hydrochloric acid; ammonia was then added and the whole concentrated to a small volume. Any precipitate that formed was filtered off; any lime present was removed as oxalate. The solution was then supposed to contain the borate together with alkali salts and was ready for the treatment with magnesium chloride solution. In regard to this method, Marignac himself says: "If good results are obtained, it is due to a balancing of errors."

Rose² substituted sodium metaborate for the sodium carbonate used in his earlier method. By fusing boric acid with calcium chloride in the presence of sodium and potassium chlorides, Ditte³ obtained the salt $\text{CaO}, \text{B}_2\text{O}_3$, which crystallized from the fusion in needles and was insoluble in cold water. He utilized this salt for the estimation of the acid. In 1877, Berg⁴ precipitated from an alcoholic solution $\text{BaO}, \text{B}_2\text{O}_3, .4\text{H}_2\text{O}$. The precipitation was fairly completed, enabling him to determine boron trioxide in borax and obtain results within one tenth per cent. to three-tenths per cent. of the theoretical amounts.

¹ *Ztschr. anal. Chem.*, (1862), 1, 405.

² *Handb. der analyt. Chemie*, 6 Aufl, 2, 721 (1871).

³ *Compt. rend.*, 80, 490 and 561 (1875).

⁴ *Ztschr. anal. Chem.*, 22, 25.

Smith¹ precipitated manganese borate, $\text{MnO} \cdot 2\text{B}_2\text{O}_3$, from a borax solution in the presence of alcohol and determined the excess of manganous sulphate added, by evaporating the filtrate from the manganese borate to dryness, taking up with water and titrating the manganese according to Volhard.

In applying this method to a silicate, the latter was fused with sodium carbonate, the melt extracted with water and the solution digested with ammonium sulphate to throw out silica and alumina. After removing these, a known amount of manganous sulphate solution with an equal volume of alcohol was added; the precipitate was removed and the manganese in the filtrate determined as above. In a tourmaline, the percentage of boric acid found by Marignac's method was ten per cent., while that found by Smith's method was nine and seven-tenths per cent. Bodewig² tried the method of Smith upon a silicate, but obtained no result.

With some success, Bodewig used Stromeyer's method in the determination of the free acid, but upon applying it to a silicate, he experienced considerable difficulty in obtaining a solution of the borate free from silica. To accomplish this, the procedure of Berzelius (use of an ammoniacal zinc oxide solution) was resorted to with a fair degree of success.

The method of Gooch and Rosenblatt appeared simultaneously in 1887. Gooch³ evaporated the solution of free boric acid to dryness with a weighed amount of lime and ignited to constant weight. The increase in weight represented boron trioxide. Rosenblatt⁴ used magnesia in place of lime. Both Gooch and Rosenblatt showed that boric acid could be completely expelled from the concentrated acid solution of a borate as the methyl ester. To accomplish this, Gooch used an apparatus consisting of a large pipette bent at one end of the bulb at a right angle and at the other like a goose neck; the end of the pipette extended into a condenser. Insoluble borates were fused with sodium carbonate; the melt was extracted with water and the solution evaporated to dryness in the bulb of the pipette, which was immersed in a paraffin bath. The residue was made acid with nitric or acetic

¹ *Am. Chem. J.*, (1882-83), 4, 279.

² *Ztschr. anal. Chem.*, 23, 149 (1884).

³ *Am. Chem. J.*, 9, 23.

⁴ *Ztschr. anal. Chem.*, 26, 21.

acid and the distillation with methyl alcohol begun; the methyl alcohol was added in portions of ten cc. The distillate was poured into a platinum dish, containing a weighed amount of lime, evaporated to dryness and ignited to constant weight; the increase in weight represented boron trioxide.

The apparatus used by Rosenblatt was more simple than that used by Gooch. It consisted essentially of an Erlenmeyer flask connected with a condenser. Rosenblatt's method differed from Gooch's only in that the ester was caught in an ammonium carbonate solution, then poured into a dish containing a weighed amount of magnesia, and evaporated to dryness.

Morse and Burton,¹ to a concentrated borax solution of small volume, added sulphuric acid to acid reaction using tropaeoline OO, as the indicator. After the addition of anhydrous copper sulphate, the resulting mass was extracted with absolute alcohol; this alcoholic solution was run into an excess of standard barium hydroxide. The excess of barium hydroxide was changed to carbonate, the whole evaporated to dryness and weighed as barium carbonate and barium metaborate, from which the boric acid was calculated. Insoluble borates were decomposed by fusion with sodium hydroxide in a nickel crucible. The extract of the fusion was evaporated to a small bulk and treated as the borax solution. By this procedure, Morse and Burton obtained from a tourmaline the following percentages of boron trioxide: 10.03 per cent., 10.08 per cent., and 10.11 per cent. Dr. Riggs obtained from the same tourmaline by a different method 10.15 per cent., 10.00 per cent., and 10.31 per cent. By means of a solution of baryta, Will² titrated boric acid.

Krüss and Moraht³ in the analysis of beryllium borate, gave the method of Stromeier preference. To the salt of the alkali metal, Parmentier⁴ added an excess of hydrochloric acid or sulphuric acid. After dividing the solution into two equal parts, he added to one methyl orange and titrated the excess of hydrochloric or sulphuric acid; to the other, litmus was added and the total acidity determined. The difference gave the boric acid.

¹ *Am. Chem. J.*, 10, 154 (1888).

² *Arch. d. Pharm.*, 225, 1101; abs. by *Ztschr. anal. Chem.*, 28, 100 (1889).

³ *Ann. Chem. (Liebig)*, 259, 184 (1890).

⁴ *Compt. rend.*, 123, 41 (1891).

Reischle¹ stated, that the color reaction of the litmus was so indistinct that he could obtain no results.

In 1893, Thompson² noticed that a boric acid solution containing thirty per cent. of glycerol could be titrated with sodium hydroxide with phenolphthalein as the indicator. Starch, glucose, and cane-sugar could be substituted for glycerol. In borax the acid was set free by hydrochloric acid using methyl orange as the indicator and the boric acid titrated by a solution of sodium hydroxide with glycerol and phenolphthalein. Thompson applied this method to boracite.

As the commercial method of estimating boron trioxide in boronatrocalcites, Le Roy³ gave the following: Decompose the mineral with dilute sulphuric acid and hydrochloric acid in a flask connected with a reflux condenser; remove the insoluble residue and precipitate the iron and aluminum as hydroxides by caustic soda. After the removal of these, the solution is made acid with hydrochloric acid and boiled to expel carbon dioxide; upon cooling, it is made up to a known volume. Twenty cc. of this solution are titrated with standard alkali and Porrier orange III, until the shade produced corresponds to the yellowish red caused by the same amount of orange III in twenty cc. of water. Another volume of twenty cc. is now titrated with alkali using orange II as the indicator, until the color is a dark-red. The difference between the two titrations indicates the boric acid present.

Schwarz⁴ suggested Congo red as an indicator to be used with hydrochloric acid. Hefelmann⁵ gave litmus the preference. Hefelmann recommends the expulsion of the boric acid by heating with ammonium fluoride and the estimation of it by difference.

Barthe⁶ used the method of Thompson with success as did also Hönig and Spitz.⁷ Insoluble silicates were fused by the latter with sodium and potassium carbonates. The melt was dissolved in water and as much ammonium chloride added as equaled the carbonates used in the fusion. The solution was then boiled

¹ *Ztschr. anorg. Chem.*, 4, 111 (1893).

² *J. Soc. Chem. Ind.*, 12, 432.

³ *Ibid.* (1893), 867.

⁴ *Pharm. Ztg.*, 32, 562 (1894).

⁵ *Pharm. Centralhalle (N. F.)*, 1894, 9, 116.

⁶ *J. Pharm. Chem.*, 20, 163 (1894).

⁷ *Ztschr. angew. Chem.*, (1896), 550.

and the precipitated silica removed. The last traces of silica were removed by Berzelius' method. After concentration to a small volume, the liquid was made acid with hydrochloric acid, boiled a few minutes to expel carbon dioxide and titrated. By this procedure, the percentage of boron trioxide found in a "Gasglühlicht-cylinder" was 5.12 per cent., while that found by difference was 5.34 per cent.

Hönig and Spitz also applied the reaction made use of by Kraut ($\text{Na}_2\text{B}_4\text{O}_7 + 2\text{NH}_4\text{Cl} = 2\text{NH}_3 + 2\text{NaCl} + 2\text{B}_2\text{O}_3$) to "Boraxkalk." The results obtained differed 0.10 per cent. to 0.30 per cent. from those gotten by their first method. In 1897, Kraut¹ employed Gooch's method successfully for the analysis of colemanite and pandermite. The apparatus used in the distillation of the ester was, however, more simple than that of Gooch. Schneider and Gaab² distilled the boric acid with alcohol and evaporated the distillate with a weighed amount of sodium carbonate.

By shaking with ether, Bellocq³ removed boric acid from other salts, and upon the evaporation of the ethereal extract obtained the trioxide.

Thaddeeff⁴ applied the Berzelius-Stromeyer method, somewhat modified, to borax. His modification consisted in adding to the potassium acetate solution containing the potassium borofluoride, 100 cc. of alcohol, 0.805 sp. gr., and allowing it to stand twelve to fourteen hours before filtering. The precipitate was washed with alcohol of the same specific gravity. By this means, results varying from 0.08 per cent. to 0.40 per cent. of the theoretical were obtained. Thaddeeff also volatilized boric acid as the methyl ester which was caught in a solution of potassium hydroxide. From this potassium borofluoride was precipitated. To facilitate the volatilization of the ester, Thaddeeff used a current of air. By this procedure, he obtained results varying from 0.01 per cent. to 0.40 per cent. of the theoretical.

INVESTIGATION.

From this review, it is apparent that, while boric acid in borax, soluble borates, and minerals not requiring fusion with alkalis

¹ *Ztschr. anal. Chem.*, 36, 165.

² *Pharm. Centralhalle*, 37, 672 (1897).

³ *Rev. Int. falsific.* 9, 119; abs. by *Ztschr. anorg. Chem.*, 380 (1897).

⁴ *Ztschr. anal. Chem.* 36, 568 (1897).

for their decomposition, is estimated with a fair degree of success, this acid, where fusion is required, is not determined with the desired accuracy. Minerals containing silica and alumina usually require fusion with sodium carbonate or caustic soda for their decomposition. The extract from this fusion is supposed to contain all the boric acid together with silicate and aluminate of soda. Digestion with ammonium chloride or sulphate is generally resorted to for the removal of the latter two. The solution is then ready for treatment according to any method applicable to borax.

The methods of Gooch, Stromeyer, and Marignac have been universally used. If Marignac's method is adopted, results are obtained about which there is more or less uncertainty. If Stromeyer's method is used, the potassium borofluoride weighs more than it should, owing to fluosilicate.¹ To avoid this silica, Wöhler² recommends evaporating the hydrochloric acid solution of the fusion to dryness, in a flask connected with a condenser, adding the distillate to the residue and filtering off the silica. By this means, silica is entirely removed, but alumina and other bases are yet to be separated, and in the removal of the alumina as hydroxide, there is a tendency on the part of the precipitate to retain boric acid.³ In the use of Gooch's method the trouble is met in weighing the lime.

It is evident from the foregoing, that the quantitative determination of this acid, where it exists in such combination as it does in tourmaline, is not attended with the most desirable results. With the hope of obtaining a more accurate and more rapid method and of casting some light, perhaps, upon the constitution of this mineral, this investigation was undertaken.

The isolation of the acid is evidently necessary for its successful determination. Its separation from these two associates, silica and alumina, is difficult, and alkalies apparently increase this difficulty; hence it was thought, if the tourmaline could be decomposed by heating with metallic magnesium or fusion with carbonates other than those of the alkalies, the isolation of the boric acid would be more readily accomplished; or if the tourmaline was fused with alkali carbonates, possibly it could be

¹ Fresenius' Quant. Chem. Anal., 424.

² (*Handb. der Mineral Analyse*, under Datbolite.)

³ Wöhler: *Ann. Chem. Pharm.*, 141, 268.

completely removed from these objectionable associates in an acid solution.

Since the volumetric method of Thompson seemed to offer the most rapid and accurate means, I decided to investigate it, with the view of utilizing it for the determination of the isolated boric acid.

DETERMINATION OF BORIC ACID IN BORAX BY THE
METHOD OF THOMPSON.

One-tenth normal hydrochloric acid solution was prepared and standardized by precipitating the chlorine with silver nitrate.

I. Ten cc. hydrochloric acid solution gave 0.1430 gram silver chloride = 0.035358 gram chlorine.

II. Ten cc. hydrochloric acid solution gave 0.1440 gram silver chloride = 0.035605 gram chlorine.

	Chlorine. Gram.
Average	0.035481
Theory	0.03545
Difference.....	0.000031

For this hydrochloric acid solution a tenth-normal caustic soda solution was prepared. A borax solution, ten cc. of which contained one gram of $\text{Na}_2\text{B}_4\text{O}_{10}\cdot 10\text{H}_2\text{O}$, or 0.03659 gram of B_2O_3 , was prepared from recrystallized borax. As nearly all glycerol is likely to be acid owing to fatty acids, it was found best to add a very small amount of water to the glycerol, then phenolphthalein, shake well, and introduce sodium hydroxide until a faint pink tinge appeared. This neutralized glycerol was kept in a well-stoppered bottle.

For the estimation of boric acid in the latter, a number of cubic centimeters of the borax solution were introduced into an Erlenmeyer flask, a few drops of methyl orange added and tenth-normal hydrochloric acid run in from a burette until all the boric acid was free; fifty cc. of the glycerol were added, together with a few drops of phenolphthalein, and the titration with tenth-normal caustic soda begun. According to the reaction $2\text{B}_2\text{O}_3 + 4\text{NaOH} = 4\text{NaBO}_2 + 2\text{H}_2\text{O}$, one cc. of tenth-normal alkali is equivalent to 0.0035 gram of boron trioxide.

The following table shows the value of this method :

No.	Taken.		Found.		
	Borax solution O.	B ₂ O ₃ Gram.	$\frac{N}{10}$ NaOH. cc.	B ₂ O ₃ Gram.	Per cent.
1	10	0.03659	10.4	0.0364	36.40
2	10	0.03659	10.5	0.03675	36.75
3	10	0.03659	10.4	0.3640	36.40
4	20	0.07318	21.0	0.0735	36.75
5	20	0.07318	20.9	0.07315	36.57
6	25	0.09147	26.1	0.09135	36.54
7	25	0.09147	26.1	0.09135	36.54
8	15	0.05488	15.7	0.05495	36.63
9	15	0.05488	15.7	0.05495	36.63
10	15	0.05488	15.6	0.0546	36.40

The atomic weights used were :

Oxygen = 16.00

Boron = 10.95

Silver = 107.97

Chlorine = 35.45

Sodium = 23.05

The theoretical percentages of the constituents of crystallized borax are :

	Per cent.
Sodium oxide	16.26
Boron trioxide	36.59
Water	47.15

Having proved the volumetric method of Thompson to give reliable results with borax, the problem of isolating the boric acid in tourmaline was taken up.

DECOMPOSITION OF TOURMALINE BY HEATING WITH METALLIC MAGNESIUM.

Two-tenths of a gram of brown tourmaline (No. 2) were heated to expel the water, mixed with half a gram of magnesium powder, the whole placed in a porcelain crucible and covered with a thick layer of thoroughly dried salt. It was then heated for thirty minutes and allowed to cool. The contents, which had the appearance of amorphous silicon, together with any parts of the crucible to which the contents adhered, were powdered, placed in a porcelain boat, and chlorine passed over the same. The chlorine and any volatile portion were caught in two U-tubes containing water; later, heat was applied and gradually raised to a dull red, where it was held until the contents of the boat became quiescent. The heat was then gradually withdrawn.

After four days, most of the chlorine had gone from the U-tubes, leaving the contents exceedingly acid. Sodium carbonate sufficient to neutralize the acid was added, and the solution evaporated almost to dryness. After making acid and expelling the carbon dioxide by drawing air through the solution for fifteen minutes, the excess of acid was neutralized by sodium hydroxide with methyl orange as the indicator, and the boric acid titrated with the following results:

No.	Weight of mineral.		$\frac{N}{10}$ NaOH. cc.	B_2O_3 . Gram.	Per cent.
	Gram.				
1	0.2000		5.0	0.0175	8.75
2	0.2000		2.5	0.00875	4.357
3	0.2000		1.2	0.0042	2.10
4	0.2000		2.0	0.007	3.50
5	0.2000		1.5	0.00525	2.625

No. 4 was allowed to stand two days before treating the contents of the U-tubes. Very little acid was present. Nos. 2, 3, and 5 were allowed to stand but a few hours before treating. Little acid was present and the chlorine was removed in each instance before the addition of the sodium carbonate, by drawing air through the tubes. It might be added, that the time of heating the mineral with the magnesium powder was varied from fifteen minutes to an hour, and in every case the contents of the crucible had the appearance of amorphous silicon.

This procedure is evidently not a success; just why, I do not know, but am inclined to believe that the boron chloride was not completely broken up when it came in contact with the water saturated with chlorine, but was carried on out with the escaping gas. It may have been that the mineral was not completely decomposed by the magnesium, but from all appearances the magnesium had entirely reduced it. At any rate, this procedure was abandoned, and the fusion of the mineral with the alkaline earth carbonates undertaken.

DECOMPOSITION OF TOURMALINE BY FUSION WITH CALCIUM CARBONATE.

Some of the very finely powdered mineral was fused with a mixture of eight times its weight of precipitated calcium carbonate and its own weight of ammonium chloride, at a low red heat for one hour, as in the J. Lawrence Smith fusion for

the alkalies; when cool the fusion was powdered, placed in a platinum dish, covered with water, and an amount of sodium carbonate introduced slightly in excess of that required. After digesting for half an hour the solution was allowed to cool and the insoluble portion was removed. To the filtrate sulphuric acid to almost neutral reaction was added. The precipitate which formed was filtered off and the solution made slightly acid. For fifteen minutes air was drawn through the solution to remove the carbon dioxide, after which the excess of acid was neutralized with caustic soda, with methyl orange as the indicator, and the boric acid titrated.

In this instance half-normal sodium hydroxide was used in the titration of the boric acid. One cc. of a half-normal alkali solution is equivalent to 0.0175 gram of boron trioxide. The results are shown in this table:

No.	Weight of mineral. Gram.	$\frac{N}{2}$ NaOH. cc.	B_2O_3 . Gram.	Per cent.
1	0.3000	2.4	0.0420	14.00
2	0.3000	2.8	0.0490	16.33
3	0.3000	3.7	0.06475	21.58

The decomposition of the mineral was complete, because all the portion insoluble in water, except silica, dissolved in hydrochloric acid. Upon allowing the titrated solutions to stand, in every case a precipitate of alumina separated. Thinking that during the boiling of the fusion with soda some alumina was dissolved, I used barium carbonate in the place of the soda and decomposed the fusion by boiling with sodium sulphate, with the hope of avoiding the solution of alumina.

That this was not a success is shown by the following:

No.	Weight of mineral (No. 2). Gram.	$\frac{N}{2}$ NaOH. cc.	B_2O_3 . Gram.	Per cent.
1	0.3000	1.5	0.02625	8.75
2	0.3000	3.3	0.05775	19.25
3	0.3000	4.3	0.07525	25.08
4	0.3000	2.6	0.0455	15.16
5	0.3000	2.1	0.03675	12.25
6	0.3000	1.85	0.3237	10.79

In every instance, after titration, a copious precipitate of alumina came down upon boiling with hydrochloric acid and adding an excess of ammonia. It is very likely that in the

digestion of the fusion with sodium sulphate, barium carbonate becomes barium sulphate and sodium carbonate is formed; this then dissolves the alumina.

I thought that possibly this alumina might be eliminated completely by adding a small quantity of ammonium sulphate to the sodium sulphate solution free from the insoluble portion, and digesting with a reflux condenser; the ammonia could easily be expelled by boiling with an excess of alkali. This was done and the following results obtained:

No.	Weight of mineral (No. 2). Gram.	$\frac{N}{2}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
1	0.5000	2.6	0.0455	9.10
2	0.5000	2.25	0.03937	7.87
3	0.5000	2.00	0.0350	7.00

Upon testing after the titration, alumina was found. The insoluble portions of some of these fusions were fused with sodium carbonate, and the boric acid therein, determined by distillation with methyl alcohol—a method which will be given later—and the following amounts found:

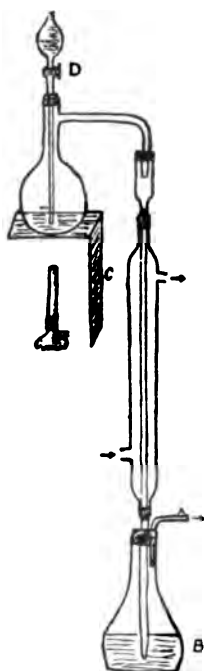
No.	Weight of mineral (No. 2). Gram.	$\frac{N}{2}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
2	0.3000	1.1	0.01925	6.41
3	0.3000	0.6	0.0105	3.50
1	0.5000	1.0	0.0175	3.50
2	0.5000	1.1	0.01925	3.85
3	0.5000	1.4	0.0245	4.90

From this it appears that the decomposition of tourmaline by fusing the mineral with calcium or barium carbonate, is not a success; nor is it a success with datolite, as the following show:

No.	Weight of mineral. Gram.	$\frac{N}{2}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
1	0.5000	4.6	0.0805	16.10
2	0.3000	2.8	0.0490	16.33

The decompositions were complete, but some boric acid had remained with the insoluble portions.

Tourmaline to be completely decomposed must be fused with alkalis. Then if boric acid is to be cleanly removed from the alumina, it must be done in an acid solution. The methods of Gooch and Rosenblatt are the only means of accomplishing this



and directly estimating the boric acid; but the process as practiced by Gooch or Rosenblatt is rather slow. Thaddeeff lessened the time necessary for the complete removal of the boric acid as the methyl ester, by using a current of air. By utilizing the discovery of Gooch and Rosenblatt and the volumetric method of Thompson, I thought a rapid and accurate method could be devised.

**THE VOLATILIZATION OF THE BORIC ACID
AS THE METHYL ESTER AND SUBSE-
QUENT TITRATION.**

To diminish the time required for the complete volatilization, an apparatus, the plan of which is here shown, was constructed. A weighed amount of fused borax was placed in the bulb, moistened with sulphuric acid, ten cc. of commercial wood alcohol added, and the distillation begun. The distillate was caught in the flask B, which contained twenty-five cc. of tenth-normal caustic soda, into which the condenser tube extended about one inch. When nearly all the alcohol had distilled over, air was drawn through the whole apparatus for a few minutes, by attaching a suction-pump to A and opening the stopcock at D sufficiently far to let the air gently bubble through the solution in B. This operation was repeated until fifty cc. of wood alcohol had been added and distilled off into the sodium hydroxide. The flask was disconnected; twenty-five cc. of tenth-normal hydrochloric acid were introduced, then 100 cc. of glycerol with a few drops of phenolphthalein and the titration of the boric acid with tenth-normal alkali begun. By this procedure the following results were obtained:

No.	Taken.		$\frac{N}{10}$ NaOH. cc.	Found.		Per cent.
	Weight of borax. Gram.	B ₂ O ₃ . Gram.		B ₂ O ₃ . Gram.		
1	0.1000	0.06924	23.00	0.0805	80.50	
2	0.1000	0.06924	22.80	0.0794	79.80	

The theoretical percentages of the constituents of fused borax are:

	Per cent.
Sodium oxide	30.76
Boron trioxide	69.24

The amount of alcohol in each case being the same and the results obtained agreeing so closely, I concluded that the alcohol was the cause of the high percentages. Upon evaporating the distillate obtained as above and igniting, a black charred mass was left, which, however, was easily burned. This showed either that some organic compound had been formed in the distillation of the alcohol from the sulphuric acid or existed as an impurity in the alcohol and was carried over during the distillation. If the substance were acetic acid or formic acid, the sodium salt would be formed, which when treated with hydrochloric acid would regenerate the acid and thus increase the amount of sodium hydroxide required.

To ascertain whether a formate was produced, some pure methyl alcohol was distilled with sulphuric acid. The distillate which was caught in caustic soda, was concentrated, the alkali neutralized with nitric acid and silver nitrate added. The odor of formic acid was distinctly perceptible upon neutralizing the sodium hydroxide, and upon adding the silver nitrate and boiling, silver separated. When the ester comes in contact with the alkali, the probable reaction is: $B(OCH_3)_3 + NaOH + H_2O = BOONa + CH_3OH$. The heating of methyl alcohol with sulphuric acid in the air seems to react thus: $CH_3OH + O_2 = H_2O + HCOOH$.

To destroy this organic acid, the distillate was evaporated to a small volume, carbon dioxide rapidly run through to insure the formation of borax, the evaporation then continued to dryness and the residue ignited until all the carbon was consumed. When cool, hydrochloric acid was added in slight excess and the carbon dioxide removed by drawing air through the solution for a quarter of an hour. The excess of hydrochloric acid was neutralized and the boric acid titrated with half-normal sodium hydroxide.

No.	Taken.		Found.		Per cent.
	Weight of borax. Gram.	B ₂ O ₃ . Gram.	$\frac{N}{10}$ NaOH. cc.	B ₂ O ₃ . Gram.	
1	0.2000	0.13848	9.0	0.1575	78.75
2	0.2000	0.13848	8.2	0.1435	71.75
3	0.1000	0.06924	4.0	0.0700	70.00

These results are too high and variable, so pure methyl alcohol was substituted for the commercial article and about sixty cc. were used each time. The boric acid was titrated in this instance with tenth-normal caustic soda. It will be noticed that sometimes tenth-normal alkali was used in the titration, and at other times half-normal. Either gave good results in the titration of boric acid in borax, but with half-normal sodium hydroxide, the end-reaction was more pronounced.

No.	Taken.		Found.		Per cent.
	Weight of borax. Gram.	B ₂ O ₃ . Gram.	$\frac{N}{10}$ NaOH. cc.	B ₂ O ₃ . Gram.	
1	0.5000	0.3462	97.5	0.34125	68.25
2	0.2000	0.13848	39.5	0.13825	69.13
3	0.3000	0.20772	58.8	0.2058	68.60

According to these reactions: $4\text{B}(\text{OH})_3 + 4\text{NaOH} = 4\text{BO}.\text{ONa} + 8\text{H}_2\text{O}$ and $4\text{BO}.\text{OH} + 4\text{NaOH} = 4\text{BO}.\text{ONa} + 2\text{H}_2\text{O}$, the treatment with carbon dioxide was unnecessary and was dispensed with in the following determinations:

No.	Taken.		Found.		Per cent.
	Weight of borax. Gram.	B ₂ O ₃ . Gram.	$\frac{N}{10}$ NaOH. cc.	B ₂ O ₃ . Gram.	
1	0.2000	0.13848	39.8	0.1393	69.65
2	0.3000	0.20772	59.4	0.2079	69.30
3	0.4000	0.27696	79.3	0.2775	69.36
4	0.2000	0.13848	39.6	0.1386	69.30

The theoretical per cent. of acid in fused borax is 69.24. This shows that this method is a good one, applied to borax. The next thing was to apply it to tourmaline.

A brown tourmaline, marked (No. 2), from McAfee, New Jersey, on analysis gave the following:

	Per cent.
Silica	33.72
Boric acid	10.00
Alumina	25.88
Ferric oxide	1.82
Ferrous oxide.....	3.23
Lime	6.92
Magnesia	14.07
Loss on ignition	1.80
Potassium oxide	0.20
Sodium oxide	2.52

In this instance, the boric acid was estimated according to

Marignac's method. The tourmaline was fused with potassium and sodium carbonates; the fusion was taken up with water, evaporated almost to dryness, then transferred to the distilling bulb together with the insoluble oxides. The distilling bulb instead of resting on an asbestos pad, was immersed to half the depth of the bulb, in a glycerine bath. The temperature of the bath was raised to 135°C . and the contents of the flask rapidly evaporated to dryness by the aid of a current of air. This required about an hour. The glycerine bath was allowed to cool down to 50°C . and a flask containing sodium hydroxide was substituted for the one previously used to catch the distillate. The contents of the bulb were made decidedly acid and the distillation with methyl alcohol commenced. The remainder of the operation was the same as with borax.

The following table shows the results of this method :

No.	Weight of mineral (No. 2).		$\frac{N}{10}\text{NaOH}$.		B_2O_3 .		Per cent.
	Gram.		cc.		Gram.		
1	0.5000		16.0		0.0560		(11.20)
2	0.5000		16.0		0.0560		(11.20)
3	1.0000		31.0		0.1085		(10.85)
4	1.0000		22.4		0.0784		(7.84)
5	1.0000		27.4		0.0959		9.59
6	0.5000		13.6		0.0476		9.52
7	0.5000		13.7		0.04795		9.59

In Nos. 5, 6 and 7, the fusion was allowed to cool completely and by rolling the crucible between the fingers with gentle pressure, the fusion dropped out. It was placed in the distilling flask, the crucible rinsed with sulphuric acid (1 : 1), and the washings added. Sulphuric acid and water sufficient to break the mass up into a mushy state, were poured over it and the distillation with methyl alcohol conducted as with the others. By the procedure used in these latter determinations, the entire time consumed was about five hours.

A black tourmaline which gave, according to Marignac's method, 9.87 per cent. of boric acid, treated by the above method gave the following :

No.	Weight of mineral.		$\frac{N}{2}\text{NaOH}$.		B_2O_3 .		Per cent.
	Gram.		cc.		Gram.		
1	0.5000		2.9		0.05075		10.15
2	0.5000		2.9		0.05075		10.15

From datolite, the following percentages were obtained :

No.	Weight of mineral.	$\frac{N}{2}$ NaOH.	B_2O_3 .	Per cent.
	Gram.	cc.	Gram.	
1	0.5000	5.50	0.09625	19.25
2	0.5000	5.55	0.097125	19.43

Another sample of a brown tourmaline marked No. 4 gave these results :

No.	Weight of material.	$\frac{N}{2}$ NaOH.	B_2O_3 .	Per cent.
	Gram.	cc.	Gram.	
1	0.5000	2.80	0.0490	9.80
2	0.5000	2.90	0.05075	10.15
3	0.5000	2.85	0.04988	9.976
4	1.0000	5.70	0.09975	9.975

In each of the preceding determinations the residue in the distilling bulb was tested for boric acid, but none was found. These results show this to be a good method of estimating boric acid wherever it is associated with silica and alumina. The time consumed is considerably less than that required by other methods, and the complete isolation of the boric acid is accomplished. The construction of the apparatus required by this method is an objection, a very slight one, however.

It occurred to me that possibly a more simple method might be found in that proposed by Smith.¹ With this in view I took up the method of Smith for investigation.

ESTIMATION OF BORIC ACID BY THE METHOD OF SMITH.

A borax solution, one cc. of which contained 0.004 gram of $Na_2B_4O_7$, a potassium permanganate solution containing zinc sulphate, one cc. of which was equivalent to 0.0018705 gram of manganese, and a manganous sulphate solution containing 0.005228 gram of manganese in each cubic centimeter, were prepared. To a volume of the manganous sulphate solution, a known portion of the borax solution, with an equal quantity of alcohol, was added. As soon as the precipitate settled it was filtered off by means of a Gooch crucible and a suction-pump. The filtrate containing the excess of manganous sulphate was evaporated to dryness, the residue gently ignited and when cool dissolved in water. A few drops of a saturated solution of sulphur dioxide were added to aid in dissolving the residue.

¹ *Am. Chem. J.*, 4, 279.

The liquid was then transferred to a flask and brought to boiling. The titration of the manganese according to Volhard's method was now made, and from this the boric acid calculated by the reaction $\text{MnSO}_4 + \text{Na}_2\text{B}_4\text{O}_7 = \text{MnB}_2\text{O}_7 + \text{Na}_2\text{SO}_4$.

No.	Borax solution. cc.	Borax. Gram.	MnSO ₄ solution. cc.	Manganese. Gram.	KMnO ₄ . cc.	Excess of Mn.	B ₂ O ₃ . Per cent.	Volume alcohol.
1	10	0.04	5	0.02614	8.0	0.014964	71.03	15
2	10	0.04	5	0.02614	8.0	0.014964	71.03	15
3	10	0.04	5	0.02614	8.2	0.015338	68.33	10
4	10	0.04	10	0.05228	22.1	0.041338	68.91	10
5	15	0.06	10	0.05228	18.9	0.035354	71.71	15
6	15	0.06	10	0.05228	19.2	0.035914	69.38	15
7	25	0.10	15	0.07842	27.3	0.051065	69.54	20
8	25	0.10	15	0.07842	27.3	0.051065	69.54	20
9	25	0.10	25	0.13071	55.3	0.10344	69.30	25
10	20	0.08	20	0.10456	43.5	(67.68)	20

The precipitate of $\text{MnO} \cdot 2\text{B}_2\text{O}_3$ was dissolved off the filter by a warm aqueous solution of sulphur dioxide, transferred to a flask, brought to boiling, and the manganese then titrated with potassium permanganate according to the method of Volhard. This was done with each precipitate with the following results:

No.	KMnO ₄ . cc.	Gram Mn with 2B ₂ O ₃ .	B ₂ O ₃ . Per cent.	Total Mn determined.	Difference from amount taken.
1	6.0	0.011223	71.31	0.026187	0.000046 plus.
2	6.0	0.011223	71.31	0.026187	0.000046 plus.
3	5.8	0.010849	68.94	0.026187	0.000046 plus.
4	5.9	0.011036	70.11	0.052374	0.000052 plus.
5	9.0	0.016834	71.31	0.052188	0.000094 minus.
6	9.0	0.016834	71.31	0.052188	0.000466 plus.
7	14.5	0.027122	68.94	0.078187	0.000236 minus.
8	14.7	0.027496	69.89	0.078561	0.000138 plus.
9	14.6	0.027310	69.41	0.130750	0.000045 plus.
10	15.0	0.028057	71.31

This shows that boric acid in borax may be successfully estimated either by the titration of the excess of manganous sulphate, which is Smith's method, or by titration of the manganese combined with boron trioxide.

For the estimation of boric acid in a tourmaline, Smith digested the extract of the sodium carbonate fusion with an amount of ammonium sulphate equivalent to the carbonate. The precipitate that formed was removed and the filtrate concentrated to twenty-five cc., after which it was treated as the borax

solution. This I did, but upon adding the manganous sulphate obtained no precipitate, and upon testing with litmus, found the liquid acid. This corroborates Bodewig's statement.¹ Another fusion was made and the extract evaporated to a volume of twenty cc., then transferred to a flask connected with a reflux condenser, and digested with ammonium sulphate. The precipitate was removed and the filtrate and washings concentrated to a volume of twenty-five cc. To the solution, which was faintly ammoniacal, a known volume of manganese sulphate, with an equal volume of alcohol, was added. As soon as the precipitate had settled it was filtered off and washed with alcohol and water (one to one). The filtrate was evaporated to dryness and the residue ignited; when cool, it was taken up with water and a drop of aqueous sulphur dioxide added. The liquid was brought to boiling and the manganese titrated with potassium permanganate. Two determinations gave respectively 23 per cent. and 28.12 per cent. of boric acid.

There is no doubt but that in the ammoniacal solution manganic hydroxide is formed and carried down with the manganese borate. I dissolved this precipitate in aqueous sulphur dioxide, and attempted to remove the manganese from the boron trioxide, in order to titrate the boron trioxide with sodium hydroxide, but could find no means of separating the two without volatilizing some boric acid or introducing harmful reagents.

My attention was next turned towards the method used by Hönig and Spitz², for the determination of boric acid in a "Gasglühlichtcylinder," with the hope of obtaining a simple method applicable to tourmaline.

THE HÖNIG AND SPITZ METHOD OF DETERMINING BORIC ACID IN INSOLUBLE SILICATES.

The extract of the fusion of a brown tourmaline was digested with an amount of ammonium chloride, equivalent to the carbonate used in the fusion, and the precipitated alumina and silica filtered off. An ammoniacal zinc oxide solution was added, and the whole boiled until all the ammonia was expelled. The zinc oxide, with any silica it carried, was removed and the filtrate concentrated to a small volume. After being made

¹ *Ztschr. anal. Chem.*, 23, 143.

² *Ztschr. angew. Chem.* (1896), 551.

slightly acid with hydrochloric acid, the solution was boiled for fifteen minutes in a flask connected with a reflux condenser; when cooled the condenser was washed out with water (the washings going into the flask), and after neutralizing the excess of hydrochloric acid, the titration for boric acid was made. The results obtained were very high, and in every instance after titration, a white precipitate which proved to be alumina and zinc oxide, separated. This further shows that boric acid cannot be separated from alumina by digestion with ammonium salts and that the removal of zinc oxide by this means is a difficult task. The following course was then pursued. After the addition of ammonium chloride, the extract of the fusion was evaporated to dryness, the residue gently ignited to expel the ammonium chloride and when cool taken up with water. Any insoluble matter was removed, a small amount of sodium carbonate added and the whole boiled for a few minutes. When cool, the carbon dioxide was expelled by adding hydrochloric acid and boiling, and the boric acid titrated after neutralizing the excess of hydrochloric acid. Tenth-normal sodium hydroxide was used with the following results:

No.	Weight of mineral (No. 2).		$\frac{N}{10}$ NaOH.		B_2O_3 .	
	Gram.		cc.		Gram.	Per cent.
1	0.2000		4.5		0.01575	7.875
2	0.5000		10.5		0.03675	7.35
3	0.5000		11.2		0.0392	7.84

These results are lower than those previously obtained in the same sample (page 875), and are due to the volatilization of some of the boric acid during the ignition necessary to completely expel the ammonium salts, and it may be that some of the acid is lost in the boiling with the ammonium salt. In commenting on the method of Smith, Bodewig¹ says that some of the boric acid resulting from the decomposition of the borax by the ammonium salt, would be volatilized in the boiling; upon testing the escaping vapor, he found it alkaline, while the solution at the same time was acid.

To determine just how much boric acid was volatilized in this way, I decomposed a solution 200 cc. in volume, containing one gram of $Na_2B_4O_7$, by distilling with ammonium chloride; the

¹ *Ztschr. anal. Chem.* (1884), 143.

solution was distilled to one-fourth its volume. The distillate contained 0.02275 gram of boron trioxide, equivalent to 2.275 per cent. of the borax or 3.29 per cent. of the total boric acid. This shows the necessity of avoiding the boiling of an ammoniacal boric acid solution.

The digestion with ammonium chloride, using a reflux condenser to prevent the loss of boric acid, was tried, but it was impossible to get rid of the silica, alumina, and ammonium salt in this manner. Evaporation to dryness and ignition seemed to be the only way to make the silica and alumina insoluble and destroy the ammonium salt.

THE USE OF LIME TO PREVENT THE VOLATILIZATION OF BORIC ACID DURING EVAPORATION.

It occurred to me that the loss of boric acid during the evaporation to dryness and subsequent ignition, might be avoided by the addition of lime. Therefore, after digesting the extract of the fusion with ammonium chloride in a flask connected with a reflux condenser, and removing the precipitate, I added lime obtained by the ignition of precipitated calcium carbonate, evaporated the whole to dryness in a platinum dish and ignited strongly. Soda in excess of the amount required by the lime, and twenty-five cc. of water were added and the whole digested for half an hour. When cool, the precipitate was removed and well washed with cold water. After concentrating the filtrate and allowing it to cool, sulphuric acid was carefully added to almost the neutral point; the precipitate that formed was filtered out, the solution made just acid and the boric acid then titrated.

The following table shows the results obtained from the brown tourmaline (No. 4), which according to the previous method (page 876) contained 9.97 per cent. of boric acid:

No.	Weight of mineral (No. 4). Gram.	$\frac{N}{2}$ NaOH. cc.	B_2O_3 . Gram.	Per cent.
1	0.5000	2.9	0.05075	10.15
2	0.5000	3.0	0.0525	10.50
3	0.3000	1.6	0.0280	9.33
4	0.3000	1.75	0.03062	10.21

In these determinations the insoluble oxides were re-fused and the extract of the fusion added to that of the first.

To ascertain whether the $\text{CaO.B}_2\text{O}_3$, formed upon the addition of lime to the ammoniacal boric acid solution, was completely decomposed by the boiling with sodium carbonate, a weighed amount of borax was subjected to the same treatment as the extract of the fusion. That the $\text{CaO.B}_2\text{O}_3$ was entirely decomposed by the boiling with soda, is proved by this table.

No.	Taken.		Found.		
	Volume of solution. cc.	Weight of borax. Gram.	B_2O_3 . Gram.	$\frac{N}{2}\text{NaOH}$. cc.	B_2O_3 . Gram.
1	10	0.01	0.006924	0.4	0.007
2	10	0.01	0.006924	0.4	0.007
3	20	0.02	0.013848	0.8	0.014

A black tourmaline, in which, as previously shown, the boric acid amounted to 10.15 per cent., yielded 9.92 per cent. when subjected to the above treatment.

Datolite gave the following :

No.	Weight of mineral. Gram.	$\frac{N}{2}\text{NaOH}$. cc.	B_2O_3 . Gram.	Per cent.
1	0.5000	5.4	0.0945	18.90
2	0.3000	3.3	0.05775	19.25

This same datolite, according to the method on page 876, contained 19.25 per cent. of boric acid.

By using barium hydroxide in place of the lime and sodium sulphate instead of the carbonate, the following results were obtained from the brown tourmaline (No. 4):

No.	Weight of mineral. Gram.	$\frac{N}{2}\text{NaOH}$. cc.	B_2O_3 . Gram.	Per cent.
1	0.3000	1.3	0.02275	7.58
2	0.3000	1.8	0.0315	10.50
3	0.3000	1.6	0.0280	9.33
4	0.2770	1.5	0.02625	9.49
5	0.5000	2.6	0.0455	9.10
6	0.5000	2.4	0.0420	8.40

In this series, the insoluble oxides were not re-fused, but were dissolved in sulphuric acid and subjected to distillation with methyl alcohol, etc., whereupon the following percentages were obtained:

No.	$\frac{N}{2}$ NaOH. cc.	B_2O_3 . Gram.	Per cent.
1	0.2	0.0035	1.16
2	0.1	0.00175	0.58
3	0.1	0.00175	0.58
4	0.05	0.000875	0.29
5	0.1	0.00175	0.58

Upon igniting the distillate of No. 6, the characteristic green flame of boron was obtained. If these percentages are added to those previously obtained, it will be noticed that it makes the boric acid found in Nos. 3, 4, and 5 respectively 9.92 per cent., 9.80 per cent., and 9.45 per cent. These numbers agree fairly closely with those obtained from the same tourmaline by the method described on page 876. From the foregoing, the necessity of re-fusing the insoluble oxides in order to entirely remove the boric acid is apparent.

This method, while not giving results as reliable as that in which the boric acid is volatilized as the methyl ester, yet answers fairly well and avoids the use of complicated apparatus: the time is lessened very little if at all. If the digestion with ammonium chloride could be avoided, that is if the alumina could be separated from the boric acid by some other means, the evaporation to dryness and ignition might be unnecessary and thus the time shortened. In looking for a means of accomplishing this object, I happened upon the reaction $2AlO.ONa + CO_2 + 3H_2O = Al_2(OH)_6 + Na_2CO_3$, which is made use of in the manufacture of soda from cryolite. Hoping by this means to separate the alumina from the boric acid, I conducted carbon dioxide into the boiling solution of the sodium carbonate fusion free from the insoluble oxides. The separation, however, was not complete, as the following show:

No.	Weight of mineral. Gram.	$\frac{N}{2}$ NaOH. cc.	B_2O_3 . Gram.	Per cent.
1	0.5000	12.0	0.2100	42.00
2	0.3000	10.0	0.1750	58.33

The solutions, after titration, were found to contain large amounts of alumina.

By passing carbon dioxide through a cold solution of sodium aluminate, Day¹ completely separated all the alumina from the

¹ *Am. Chem. J.*, 19, 718.

soda. I then passed carbon dioxide through the cold fusion extract, as shown in this table :

Time of conducting CO ₂ through the solution. Hours.	Volume of solution. cc.	
2.5	200	a precipitate formed.
2.0	300	" " "
1.0	350	" " "
2.0	500	no " "

7.5 total time. Temperature of solution 1° C.

The solution was then evaporated to a small volume, and after the expulsion of all the carbon dioxide, titrated for boric acid.

No.	Weight of mineral (No. 4). Gram.	$\frac{N}{2}$ NaOH. cc.	B ₂ O ₃ . Gram.	Per cent.
I	0.3000	1.95	0.03413	11.34

. After titration, upon boiling with hydrochloric acid and adding ammonia, a precipitate of alumina was obtained which weighed 0.0039 gram, equivalent to 1.3 per cent. of the mineral.

This procedure was then repeated with the following results :

Time of conducting CO ₂ through the solution. Hours.	Volume of solution. cc.	
2.0	300	a precipitate formed.
4.6	400	" " "
1.0	500	no " "

7.0 total time. Temperature of solution, 1° C.

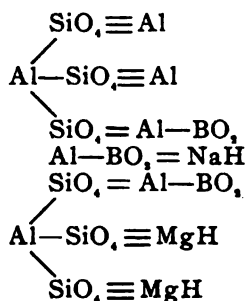
The treatment was as in the former case and 12.77 per cent. of boric acid was found. Upon testing the titrated solution for alumina, 0.0075 gram, equivalent to 1.5 per cent. of the mineral, was obtained.

In all attempts to determine the boric acid in tourmalines containing much alumina great difficulty has been experienced in separating the alumina from the boric acid and alkali carbonate. In following out Marignac's method, alumina is always found with the magnesium borate, magnesium chloride, and silica. The tenacity with which boron oxide and alumina hold to one another in other than acid solutions, is extremely great, as has already been demonstrated and is further shown by the following experiment :

0.1733 gram of aluminum, corresponding to 0.32565 gram of aluminum trioxide, was dissolved in hydrochloric acid and the

excess of acid expelled; 2.019 grams of fused borax and 1.0 gram of sodium carbonate dissolved in water, were added to the aluminum chloride and the whole boiled one hour. These proportions were taken from the equation $3\text{H}_2\text{O} + 3\text{Na}_2\text{B}_4\text{O}_7 + \text{Al}_2\text{Cl}_6 = \text{Al}_2(\text{OH})_6 + 6\text{NaCl} + 2\text{B}_2\text{O}_3$. The precipitated alumina was well washed, dissolved in hydrochloric acid, reprecipitated by ammonia, ignited, and weighed. It equaled 0.2906 gram, or 89.23 per cent. of all the alumina present in the solution. The washings, after boiling to expel the ammonia, were added to the filtrate. The volume of the solution then equaled 400 cc., and when cooled to 1°C . carbon dioxide was conducted through it for fifteen hours. The precipitate was removed and treated as the first; it amounted to 0.0332 gram, or 11 plus per cent. of all the alumina. This with the former percentage equals 100.23 per cent. Carbon dioxide, passed through two hours longer, caused no further precipitation, yet upon acidifying, then adding ammonia, a precipitate was obtained which amounted to 0.0051 gram of aluminum trioxide, or 1.56 per cent. The total amount of aluminum trioxide was 0.32565 gram, while that estimated equaled 0.3289 gram. This excess is due beyond a doubt to the contamination of the precipitates with boric acid, although in all except this last instance the precipitates were dissolved in hydrochloric acid and reprecipitated by ammonia.

The obstinacy with which aluminum trioxide and boron trioxide cling together, it seems to me, would indicate the existence of a salt of aluminum and boron in this alkaline solution. This would also favor the view held by Clarke (Bulletin 125, United States Geological Survey), which he expresses in his structural formula for toufmaline.



The alumina, as is seen, links the boric acid to the silica. This view, I think, is further strengthened by the fact that calcium or barium carbonate, fused with borax, then boiled with sodium carbonate or sulphate, gave up all the boron trioxide to the alkali, while tourmaline, heated with calcium or barium carbonate, then boiled with carbonate or sulphate of soda, yielded to the alkali but a portion of the boric acid; the alumina most likely held the remainder.

SUMMARY.

In order to avoid the introduction of alkalies, which, as it has been shown, are objectionable, new methods for the decomposition of the mineral were attempted. The first of these was the heating of the mineral with metallic magnesium and subsequently volatilizing the boron by heating in a stream of chlorine. From all appearances, the decomposition of the mineral was complete, but in the treatment with chlorine, either the boron was partially retained by the other chlorides formed at the same time, or if it was entirely volatilized as the chloride, it was not decomposed when it came in contact with the water saturated with chlorine. By using a large volume of water this difficulty might be avoided, but if the chlorine is removed by drawing air through the solution, some boric acid would be carried out with it. Again, if alkali is added, hypochlorite of the alkali would be formed, and this, when neutralized, would free chlorine, which again would likely carry with it boric acid, or the hypochlorous acid formed would cause trouble in the titration.

By fusing the mineral with calcium carbonate, also with barium carbonate, a complete decomposition was obtained, but the separation of the boric acid was incomplete. Some of the boric acid was held by the alumina, which was re-fused to yield it to the alkali with which the fusion was digested. This must be the case, since calcium or barium carbonate fused with borax, then boiled with sodium carbonate or sulphate, gave up all the boron trioxide. This strengthens the idea that the boron, which is so constant a quantity in tourmalines, is linked through the aluminum to the silica, probably as an aluminum metaborate, as Clarke suggests.

The mineral was then fused with alkali carbonates, and by volatilizing the boron from an acid solution as the methyl ester, the boron was successfully isolated and its estimation made by the volumetric method of Thompson. The use of a current of air with the apparatus described, shortens the time required for the volatilization of the ester, very materially. As has been shown, impure methyl alcohol prevents the complete volatilization of the boric acid. The results obtained by this method are reliable, and the method is capable of very wide application. The great affinity that alumina has for boric acid, has been pretty thoroughly demonstrated in the foregoing work, and the most successful means of overcoming this affinity and completely separating these two, is by volatilizing the boric acid from an acid solution. If an acid or ammoniacal borax solution is boiled, there is the likelihood of a very appreciable loss of boric acid; by this method there is no boiling of acid or ammoniacal solutions. These facts, and the brief time required for its performance, recommend this method for the estimation of boric acid in all silicates.

Could boric acid be separated from manganese, without volatilization, its estimation in silicates could be accomplished through the salt $\text{MnO} \cdot 2\text{B}_2\text{O}_3$. As has already been proved, the method is successful when applied to borax. If the attempt is made to remove the manganese with alkali, the precipitation is incomplete; if ammonium sulphide is used, the difficulties encountered are well known, and if the manganese is precipitated from an acid solution, boric acid is volatilized.

As has been shown, the volatility of boric acid in ammonia is very appreciable, hence any method in which an ammoniacal boric acid solution is boiled in the open, is unreliable, unless some substance is introduced to bind the acid. I have used lime for this purpose, and found it to fulfil its end.

By re-fusing the insoluble oxides with alkali carbonate, it is possible to separate the boric acid. However, I do not believe the separation is complete even then, but that the amount of boric acid left after the first fusion is so diluted by the second, that what remains with the insoluble oxides may be neglected. By twice fusing and digesting the extract with ammonium chloride with a reflux condenser, then evaporating the solution

to dryness with lime in a platinum dish and igniting the residue, the silica and alumina are made insoluble; then digestion with sodium carbonate gives borax in which the boric acid is readily titrated by the method of Thompson. This method works very well with alumina containing silicates; with datolite, better results were obtained. It avoids the use of complicated apparatus and requires for its execution about four hours. With silicates decomposable by digestion with acids' it seems to me, this would be the method.

The obstinacy that is encountered in separating alumina from boron trioxide in an alkaline solution, calls to my mind a point which I think is worthy of some attention. In the complete analysis of minerals, such as tourmaline, it is customary to evaporate the hydrochloric acid solution of the fusion to dryness, remove the silica and precipitate the iron and alumina from the filtrate as hydroxide by ammonia. Although these hydroxides have been dissolved in hydrochloric acid and reprecipitated, yet considerable difficulty is experienced in obtaining two determinations from the same sample that agree. This trouble I believe to be due to boric acid, which does not go off in the evaporation to dryness with hydrochloric acid. If this be true, this difficulty might be eliminated by the addition of methyl alcohol during the evaporation with hydrochloric acid.

The facts to which I have called attention in the latter part of this paper, argue strongly for the formula proposed by Clarke to represent the structure of tourmaline. But, as I have said, we know nothing of the magnitude of the molecule, hence such representations are surmises only. Until some means of ascertaining the size of the mineral molecule has been devised, such formulas will have to be looked upon with doubt.

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AN ELECTROLYTIC STUDY OF BENZOIN AND BENZIL.¹

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INTRODUCTION.

AS is well known, there is a wide difference in the action of various oxidizing as well as reducing agents on organic compounds. Probably no better illustration could be given of this than the following, on the oxidation of aniline, from Lassar-Cohn's "Manual of Organic Chemistry:" "With manganese dioxide and sulphuric acid, aniline gives ammonia and very little quinone. Chromic acid mixture gives a quantitative yield of the latter. Potassium permanganate in alkaline solution gives azobenzene, ammonia, and oxalic acid. In acid solution it gives aniline black, which with more energetic oxidation, is converted into quinone. In neutral solution, nitrobenzene and azobenzene are the chief products. Boiling bleaching-powder solution likewise gives nitrobenzene. Hydrogen peroxide in presence of weak acids gives ammonia and dianilidobenzoquinone anilide. In presence of strong acids it seems to give an inuline derivative."

In like manner, there is a marked difference in effect between electrolytic oxygen and hydrogen and other oxidizing and reducing agents. And again, different degrees of oxidation or reduction by the current can be effected by variations in current density, concentration, temperature, etc.

To study the oxidizing and reducing action of the electric current on benzoïn and benzil as compared with other agents, and to determine the result of working in different solutions as well as with variations in current density, concentration, and temperature, is the object of this investigation.

The apparatus with which the experiments were performed consisted of a beaker-glass, a porous cup, which separated the anode and cathode liquids, and platinum electrodes, each of 100 sq. cm. surface. When hydrochloric acid solutions were used the platinum anode was replaced by one of carbon.

When heat was applied in sufficient amount to evaporate the

¹ From author's thesis for the degree of Ph.D.

solvent, the top of the porous cup was closed by a rubber stopper, carrying, besides a heavy platinum wire to which was attached the electrode, a tube which led the vapor to a return condenser.

In some of the experiments with alkaline solutions the porous cup was replaced by a bag made of two thicknesses of heavy unbleached muslin, which had been previously soaked in concentrated caustic soda for twenty-four hours.

The outer liquid, whether an oxidation or reduction was being made, consisted of a solution of from ten per cent. to twenty per cent. of the same acid or alkali used in the inner cup.

The solvent generally used throughout this set of experiments was ninety-three per cent. ethyl alcohol. The concentration of the solutions was nearly always kept close to the point of saturation.

The current used for most of the work was that of the ordinary 110 volt incandescent light circuit; this was regulated by means of lamps and wire resistance, so that any current from one-tenth to ten amperes could be used. In a few instances the current from storage cells was used.

The melting-points given in the following work were taken with an ordinary thermometer and are not corrected.

EXPERIMENTS ON THE ELECTROLYTIC OXIDATION OF TOLUENE.

Before taking up the work on the oxidation and reduction of benzoin, attempts were made to oxidize the methyl group in toluene by the action of electrolytic oxygen. These experiments were unsuccessful, but it is hoped that they may not be without some interest.

The toluene used was from Kahlbaum, and distilled constantly at 110°.

Experiment I.—

15 grams toluene.

210 cc. alcohol.

15 grams sodium hydroxide.

30 cc. water.

N.D.₁₀₀ = 0.05 ampere.

Voltage = 60–70.

Temperature, 20°.

Time, 1 hour.

On acidifying the cup contents with hydrochloric acid and filtering off the sodium chloride, the remaining liquid, on distillation, yielded nothing but alcohol, water, and toluene, together with a small amount of brown resin.

Experiment II.—

33 grams toluene.
460 cc. alcohol.
65 cc. water.
30 grams sodium hydroxide.

N.D.₁₀₀ = 0.05 ampere.
Voltage = 2½.
Temperature, 25°.
Time, 1 hour.

The alcohol was distilled from the anode liquid and hydrochloric acid added to acidulation. This acid liquid, on shaking with ether, gave nothing but toluene and a small amount of resinous material.

Experiment III.—

15.4 grams toluene.
210 cc. alcohol.
15 grams sodium hydroxide.
30 cc. water.

N.D.₁₀₀ = 0.25 ampere.
Voltage = 40-50.
Temperature, 20.5°.
Time, 10 hours.

There was no heat applied and the current produced no rise in temperature. The cup contents were acidified with hydrochloric acid and the sodium chloride which separated filtered off; subsequent distillation yielded only water, alcohol, and toluene, besides a small amount of brown resinous substance.

Experiment IV.—

63.7 grams toluene.
30 cc. acetone.
Sodium hydroxide to saturation.

N.D.₁₀₀ = varying.
Voltage = varying.
Temperature, varying.
Time, 2 hours.

On connecting the poles in circuit it was found that this solution would not conduct the current, so one cc. of a saturated solution of sodium hydroxide was added. The current was started at a normal density of 4.25 amperes and voltage of 13; after fifteen minutes the heat developed by the current was sufficient to make the acetone boil violently. The current was lowered to two and five-tenths amperes, the acetone still continuing to boil. In one hour and twenty minutes the temperature in the outer cup was 68°, and twenty minutes later one cc. of a saturated solution of sodium hydroxide was added. At the end of two hours the amperage had fallen to one and the voltage stood at seventy.

The anode liquid, on distilling off the acetone, yielded nothing but a small amount of tarry substance. This experiment showed that acetone would not serve as a solvent.

Experiment V.—

42.5 grams toluene.
20 grams sodium sulphate.
100 cc. alcohol.

N.D.₁₀₀ = 0.5 ampere.
Voltage = 12-20.
Temperature, 25°.
Time, 9½ hours.

The alcohol and part of the toluene were removed by distillation and the anode liquid was then neutralized with barium carbonate. The neutral solution was shaken out with ether and this extract yielded, on fractionation, besides toluene, less than one cc. of a liquid of ester-like odor, which boiled between 39° and 44° under a pressure of twenty mm. The barium carbonate residue contained no organic products.

Experiment VI.—

42.5 grams toluene.
50 cc. alcohol.
4 grams sodium sulphate.

N.D.₁₀₀ = 0.5 ampere.
Voltage = 80.
Temperature, 75°.
Time, 12 hours.

The current heat held the temperature at 75°. After twelve hours a strong-smelling layer of brown oily liquid separated on the top of the solution in the porous cup. This, on being neutralized with sodium carbonate and shaken out with ether, gave on fractionation a small amount of a liquid similar in odor to that obtained in the previous experiment, and which distilled under twenty mm. pressure almost constantly at 35°. Too small an amount of this was obtained to determine its composition. The residual liquid gave no organic products on being reacidified.

Experiment VII.—

42.5 grams toluene.
100 cc. alcohol.
10 grams ammonium sulphate.

N.D.₁₀₀ = 1 ampere.
Voltage = 40-50.
Temperature, 75°-80°.
Time, 9½ hours.

During the electrolysis a very strong odor like that of impure acetamide was observed. After nine and one-half hours the current was interrupted and the upper oily layer which had separated, neutralized and dried over calcium chloride. On subjecting this liquid to fractionation, besides toluene and tarry matter, a very small amount of a sharp smelling substance was obtained, which distilled under seventy mm. pressure at 39°-42°.

It was then determined to increase the amperage, to see if a definite product could be obtained in some quantity.

Experiment VIII.—

42.5 grams toluene.

100 cc. alcohol.

10 grams ammonium sulphate.

N.D.₁₀₀ = 1.5 amperes.

Voltage = 11-14.

Temperature, 60°-65°.

Time, 9½ hours.

As in the previous experiment, a strong odor like that of impure acetamide was observed. The anode liquid was neutralized by standing twelve hours over barium carbonate. On shaking out with ether and fractionating nothing but tarry products could be obtained. The residual liquid gave no organic products on being acidulated and shaken out with ether.

No further work was done in this direction, the oxidation of benzoïn being taken up next.

Since a mixture of chromic and nitric acids readily oxidizes the methyl group in toluene to carboxyl, doubtless conditions can be found in which the same would be effected by electrolytic oxygen. The great obstacle in the above work was in obtaining a solvent that would give a solution of low resistance, and at the same time dissolve a sufficient amount of toluene. When such a solution is obtained the current density could certainly be found with which the desired oxidation would be accomplished.

ELECTROLYTIC OXIDATION OF BENZOIN.

The benzoïn for the following experiments was prepared by treating 230 grams of benzaldehyde with 460 grams alcohol, 46 grams potassium cyanide, and 115 grams water. This solution was boiled under a return condenser on the water-bath for one hour. The crystals which separated on cooling were washed with cold alcohol, treated with bone-black in boiling alcohol, and the solution filtered and recrystallized. The crystals thus prepared melted at 134°.

In the work with benzoïn both the oxidizing and reducing effects of the current were studied.

Oxidation of Benzoïn in Alcoholic Sodium Hydroxide Solution.—

The first experiment was made with an alkaline alcoholic solution of benzoïn, the conditions being taken at random.

Experiment I.—

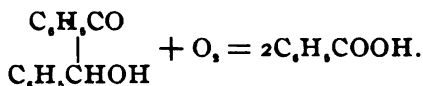
5 grams benzoin.
 5 grams sodium hydroxide.
 200 cc. alcohol.

N.D₁₀₀ = 0.75 ampere.
 Voltage = 3.8
 Temperature, 60°.
 Time, 7 hours.

It was found necessary with the above proportions to heat the alcohol to 60° in order to keep the benzoin in solution; this was done by placing the beaker containing the porous cup on a water-bath. At the end of seven hours the anode liquid had an acid-reaction. Hydrochloric acid was added to set free any organic acid that had been formed, and the liquid shaken out with ether. The ethereal extract, on evaporation, left a solid mass of an impure crystalline body. This was boiled up with barium carbonate and water, filtered, acidified, shaken out with ether, and the residue on sublimation gave crystals resembling benzoic acid, having a melting-point of 121.5°. An analysis of these crystals gave the following:

Weight of substance in gram.	Weight of CO ₂ .	Per cent. C.	Per cent. C calculated for C ₆ H ₅ COOH.
0.155	0.3875	68.11	68.85
	Weight of H ₂ O.	Per cent. H.	Per cent. H calculated for C ₆ H ₅ COOH.
	0.071	5.08	4.91

This identifies the body as benzoic acid, the oxidation proceeding according to the equation:



Besides the benzoic acid there was a large quantity of tarry decomposition product formed in this as well as in the following experiments.

The benzoic acid obtained was not weighed and the following experiments, II to VII inclusive, were made to find the conditions giving the best yield of benzoic acid.

The quantity of sodium hydroxide was increased because, as was noted above, the cup contents had an acid-reaction at the close of Experiment I.

Experiment II.—

5 grams benzoïn.
10 grams sodium hydroxide.
200 cc. alcohol.

N.D.₁₀₀ = 0.5 ampere.
Voltage = 4.5.
Temperature, 60°.
Time, 7 hours.

The anode liquid was still alkaline at the end of the time. The alcohol was evaporated, the residual liquid acidified with hydrochloric acid, shaken out with ether and the residue sublimed. A yield of sixteen per cent. of benzoic acid was obtained.

In the next experiment the amperage required by theory to convert all the benzoïn to benzoic acid, was conducted through the solution.

Experiment III.—

5 grams benzoïn.
10 grams sodium hydroxide.
250 cc. alcohol.

N.D.₁₀₀ = 0.5 ampere.
Voltage = 3.8.
Temperature, 60°.
Time, 5 hours.

The anode liquid subjected to the same treatment as before gave 9.6 per cent. of benzoic acid.

In the next experiment the time was shortened and a marked decrease in yield noted.

Experiment IV.—

5 grams benzoïn.
10 grams sodium hydroxide.
250 cc. alcohol.

N.D.₁₀₀ = 0.5 ampere.
Voltage = 4.5.
Temperature, 60°.
Time, 3 hours.

The quantity of benzoic acid obtained was 8.2 per cent. In the next experiment the concentration was increased and the normal density lowered.

Experiment V.—

5 grams benzoïn.
10 grams sodium hydroxide.
150 cc. alcohol.

N.D.₁₀₀ = 0.25 ampere.
Voltage = 2.8.
Temperature, 60°.
Time, 7 hours.

These conditions gave eighteen per cent. of benzoic acid, the largest yield obtained by oxidation in alkaline solution.

In the following experiment the concentration and normal density were made the same as above and the time shortened.

Experiment VI.—

5 grams benzoin.
10 grams sodium hydroxide.
150 cc. alcohol.

N.D.₁₀₀ = 0.25 ampere.
Voltage = 2.8
Temperature, 60°.
Time, 5 hours.

The yield of benzoic acid in this case was 14.8 per cent.

To try the effect of higher amperage and longer time, both these factors were made twice as great as in Experiment V.

Experiment VII.—

5 grams benzoin.
10 grams sodium hydroxide.
150 cc. alcohol.

N.D.₁₀₀ = 0.5 ampere.
Voltage = 4-5.
Temperature, 60°.
Time, 14 hours.

The yield of benzoic acid obtained was 17.4 per cent. showing that no improvement was made by increasing time and normal density over that of Experiment V.

*Oxidation of Benzoin in Alcoholic Sulphuric Acid Solution.**Experiment I.—*

5 grams benzoin.
5 grams sulphuric acid (conc.).
110 cc. alcohol.

N.D.₁₀₀ = 0.25 ampere.
Voltage = 2.6.
Temperature, 60°.
Time, 7 hours.

On evaporating off about three-fourths of the alcohol from the anode liquid and cooling, crystallization set in. The crystalline mass was filtered off, washed with alcohol, redissolved in boiling alcohol and treated with bone-black; when cool, white crystals separated which gave a melting-point of 134°, proving the substance to be unchanged benzoin.

The concentration, time, and normal density were increased in the next experiment in order to effect the oxidation.

Experiment II.—

5 grams benzoin.
5 grams sulphuric acid (conc.).
100 cc. alcohol.

N.D.₁₀₀ = 0.5 ampere.
Voltage = 3.8.
Temperature, 60°.
Time, 10 hours.

The anode liquid was neutralized with sodium carbonate, after having the greater part of the alcohol removed by evaporation; a layer separated at this point having the odor of ethyl benzoate.

This ester layer was separated, and distilled between 200° and 215° ; its saponification yielded benzoic acid. The lower layer after the removal of the ester was extracted with ether, the solvent evaporated, and the residue sublimed. This gave one and a half per cent. of benzoic acid, while the ester above held 15.8 per cent. in combination, making a total yield of 17.3 per cent.

The analysis of this acid gave the following:

Weight of substance in gram.	Weight of CO_2 .	Per cent. C.	Per cent. of C calculated for $\text{C}_6\text{H}_5\text{COOH}$.
0.3960	0.9975	68.69	68.85
	Weight of H_2O .	Per cent. of H.	Per cent. of H calculated for $\text{C}_6\text{H}_5\text{COOH}$.
	0.181	5.07	4.91

The residue from the ether extract above was of a yellow color, which could be removed by chloroform, but on evaporation only a tarry mass was left.

The effect of an increase in normal density was tried in the next experiment, the other factors remaining the same.

Experiment III.—

5 grams benzoïn.
5 grams sulphuric acid (conc.).
100 cc. alcohol.

N.D.₁₀₀ = 1.5 amperes.
Voltage = 9-10.
Temperature, 60° .
Time, 10 hours.

The anode liquid, worked up as before, gave for the total of free benzoic acid and that combined as ethyl benzoate only two and eight-tenths per cent. The quantity of tarry matter present was larger than in any previous experiment of this series.

Oxidation of Benzoïn in Alcoholic Hydrochloric Acid Solution.—

For the following experiments an anode of carbon was used together with a porous cup similar to that of the previous line of experiments. The outer liquid was a twenty per cent. hydrochloric acid solution. As benzoic acid resulted from the above oxidations, it was believed that it might be possible to prepare a chlorinated benzoic acid by working with a hydrochloric acid solution. The reaction, however, took a different course as the following experiments show:

Experiment I.—

5 grams benzoïn.
20 cc. hydrochloric acid (conc.).
100 cc. alcohol.

N.D.₁₀₀ = 1 ampere.
Voltage = 2.3.
Temperature, 60° .
Time, 9 hours.

On account of the size of the carbon electrode the anode chamber was left open and the alcohol, that escaped by evaporation, replaced from time to time.

When the cup contents cooled, a mass of ill-defined crystals separated. The supernatant liquid was decanted, the mass washed with cold alcohol and dried. The substance was then sublimed, giving crystals resembling benzoic acid; these were subjected to two more sublimations, then dissolved in sodium carbonate, and reprecipitated; a final sublimation yielded crystals which melted at 121° . A yield of three and two-tenths per cent. of benzoic acid was obtained.

A small amount of a yellow solid separated from the supernatant liquid on the removal of the alcohol. This same yellow body separated from the benzoic acid at the point in its purification where it was treated with sodium carbonate solution. The two portions were combined, dissolved in alcohol, treated with bone-black, filtered, and recrystallized, giving a melting-point of 94° . Not enough of this body was obtained at this point for analysis, but as will be seen in the succeeding experiments, it proved to be benzil, and changes in the working conditions produced it with no accompanying yield of benzoic acid.

The analysis of the above acid gave the following:

Weight of substance in gram.	Weight of CO_2 .	Per cent. C.	Per cent. C calculated for $\text{C}_6\text{H}_5\text{COOH}$.
0.165	0.420	69.83	68.85
	Weight of H_2O .	Per cent. H.	Per cent. H calculated for $\text{C}_6\text{H}_5\text{COOH}$.
	0.0825	5.58	4.91

Experiment II.—

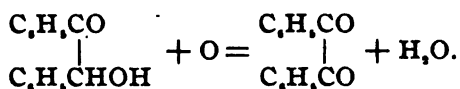
5 grams benzoin.
25 cc. hydrochloric acid (conc.).
150 cc. alcohol.

N. D.₁₀₀ = 2 amperes.
Voltage = 3.
Temperature, 60° .
Time, 12 hours.

When the cup contents cooled some benzoin crystallized out. The liquid had a strong odor of ethyl acetate. On evaporating off the alcohol and ethyl acetate an oily substance separated, which solidified when the residual liquid cooled; this was removed, dissolved in alcohol, treated with bone-black, and allowed to crystallize; the body thus obtained gave a melting-point of 94° . The analysis of this body gave the following:

Weight of substance in gram.	Weight of CO ₂ .	Per cent. of C.	Per cent. of C calculated for C ₁₄ H ₁₀ O ₂ .
0.161	0.463	79.04	80.00
	Weight of H ₂ O.	Per cent. of H.	Per cent. of H calculated for C ₁₄ H ₁₀ O ₂ .
	0.0655	4.52	4.76

This analysis, together with the properties of the body, identify it as benzil, C₁₄H₁₀O₂. The oxidation in hydrochloric acid solution then proceeds according to the equation :



No benzoic acid could be found among the products of the oxidation.

Experiment III.—

5 grams benzoïn.
60 cc. hydrochloric acid (conc.).
140 cc. alcohol.

N.D.₁₀₀ = 3 amperes.
Voltage = 2.7.
Temperature, 70°–75°.
Time, 10 hours.

The anode liquid worked up as in the preceding experiment gave seven and five-tenths per cent. of benzil, and a careful examination failed to show any benzoic acid.

In the next experiment the quantity of hydrochloric acid was decreased and the temperature raised to 75°–80°.

Experiment IV.—

5 grams benzoïn.
25 cc. hydrochloric acid (conc.).
150 cc. alcohol

N.D.₁₀₀ = 3 amperes.
Voltage = 2.8–3.
Temperature, 75°–80°.
Time, 10 hours.

The porous cup was connected with an inverted condenser, yet at this temperature some of the alcohol escaped through the part of the cup above the line of the liquid, necessitating additions from time to time.

When the cup contents cooled, benzoïn to the amount of thirty-one per cent. crystallized out. The yield of benzil in this experiment, based on the amount of benzoïn decomposed, was 28.3 per cent.

The effect of increased normal density was tried in the following experiment:

Experiment V.—

5 grams benzoin.
25 cc. hydrochloric acid (conc.).
150 cc. alcohol.

N.D.₁₀₀ = 6 amperes.
Voltage = 4.3.
Temperature, 75°–80°.
Time, 10 hours.

As in Experiment IV considerable benzoin separated from the anode liquid on cooling. The yield of benzil here, based on the amount of benzoin decomposed, was sixty-two per cent.

The effect of a still greater normal density, together with an increase in the amount of hydrochloric acid, was tried in the next experiment.

Experiment VI.—

2.5 grams benzoin.
50 cc. hydrochloric acid (conc.).
125 cc. alcohol.

N.D.₁₀₀ = 8 amperes.
Voltage = 4.6.
Temperature, 68°.
Time, 10 hours.

No heat was applied to the solution, that developed by the current holding the temperature nearly constant at 68°. No benzoin remained over in this experiment and the yield of benzil was 75.4 per cent.

Since in none of the above experiments was there any chlorinated product, the following conditions were tried to prepare such a body:

Experiment VII.—

2.5 grams benzoin.
100 cc. hydrochloric acid (conc.).
100 cc. alcohol.

N.D.₁₀₀ = 6 amperes.
Voltage = 5–6.
Temperature, 65°–70°.
Time, 19 hours.

A dark brown pasty mass separated on cooling the anode liquid. The residual liquid after evaporation of the alcohol, deposited more of a similar material. Sublimation was tried with some of this tarry product, but no well-defined body could be obtained. Various attempts to isolate a definite product from this pasty mass resulted in failure.

ELECTROLYTIC REDUCTION OF BENZOIN.

With the exception of a small quantity of a substance melting at 205°–206°, obtained both in hydrochloric and sulphuric acid solutions, the following experiments led to no definite results.

*Reduction of Benzoïn in Alcoholic Sodium Hydroxide Solution.**Experiment I.—*

5 grams benzoïn.
5 grams sodium hydroxide.
150 cc. alcohol.

N.D.₁₀₀ = 0.5 ampere.
Voltage = 3.6.
Temperature, 60°.
Time, 10 hours.

The cathode liquid was neutralized with hydrochloric acid, the alcohol removed by evaporation, some water added, and the whole shaken out with ether. The ethereal extract yielded a very small quantity of a white crystalline substance, which on purification melted with decomposition at 204°–210°.

Experiment II.—

5 grams benzoïn.
5 grams sodium hydroxide.
200 cc. alcohol.

N.D.₁₀₀ = 4 amperes.
Voltage = 6–7.
Temperature, 70°–75°.
Time, 15 hours.

The above temperature was produced by the heating effect of the current alone. The cathode liquid was neutralized with hydrochloric acid, and the alcohol removed. From the residual liquid, on cooling, a yellow pasty substance separated together with a mass of white needle-like crystals resembling benzoic acid. The latter were separated, and purified by dissolving in sodium carbonate solution, reprecipitated by hydrochloric acid and sublimed; the product gave a melting-point of 121°, and agreed with benzoic acid in all its properties. The yield of benzoic acid was 4.9 per cent.

The yellow pasty substance resisted all attempts at crystallization, though all the solvents at hand were tried.

Experiment III.—

2.5 grams benzoïn.
5 grams sodium hydroxide.
100 cc. alcohol.
25 cc. water.

N.D.₁₀₀ = 4 amperes.
Voltage = 7
Temperature, 70°–78°.
Time, 10 hours.

The current heat in this experiment kept the temperature between 70° and 78°. A new porous cup was used and much trouble was caused by the accumulation of silicic acid between the anode and the cup. The current was stopped every two hours in order that this gelatinous mass might be removed.

The cathode liquid on standing over night separated into two layers; the whole was neutralized with hydrochloric acid and the alcohol evaporated. The residual liquid, on cooling, deposited a dark pasty mass, which on being removed dissolved in alcohol, imparting a purple color to the solution. It was found on evaporating this solution to crystallization, that a white flocculent mass separated, portions of which, exposed to the air, oxidized to a purple color like that of the alcoholic solution. Not enough of this material could be obtained in a pure state for analysis. The purple alcoholic liquid on complete evaporation left a blue mass which on sublimation gave benzoic acid.

Experiment IV.—

2.5 grams benzoïn.

5 grams sodium hydroxide.

100 cc. alcohol.

N.D.₁₀₀ = 4 amperes.

Voltage = 4.

Temperature, 50°–55°.

Time, 9 hours.

The heat of the current kept the temperature between 50° and 55°.

Nothing separated from the cathode liquid on standing, but when neutralized with hydrochloric acid a flocculent precipitate separated; this was filtered off, washed with water to free it from sodium chloride, and dissolved in alcohol; several attempts were made to crystallize it, but this could not be effected. No well-defined body could be isolated from the filtrate above after the removal of the alcohol.

The formation of benzoic acid in Experiments II and III probably resulted from air-oxidation of the unstable reduction products after their removal from the porous cup.

Reduction of Benzoïn in Alcoholic Sulphuric Acid Solution.

Experiment I.—

5 grams benzoïn.

5 grams sulphuric acid (conc.).

100 cc. alcohol.

N.D.₁₀₀ = 1.5 amperes.

Voltage = 3.6.

Temperature, 70°.

Time, 10 hours.

The cathode liquid was shaken out with ether, and this extract crystallized from alcohol after treatment with bone-black. After a second crystallization the body melted with decomposition at 235°. Not enough of this substance was obtained for analysis.

In the next experiment the temperature was increased.

Experiment II.—

5 grams benzoïn.	N.D. ₁₀₀ = 1.5 amperes.
5 grams sulphuric acid (conc.).	Voltage = 4.6.
100 cc. alcohol.	Temperature, 75°–78°.
	Time, 10 hours.

A crystalline mass lined the sides of the vessel when the cathode liquid had cooled. A purification of this material yielded a very small amount of a white substance, consisting of minute crystals which melted between 205° and 206°. Such a small quantity of this body was obtained that the analytical results can have but little value. The figures obtained are as follows:

Weight of substance in gram.	Weight of CO ₂ .	Per cent. C.	Weight of H ₂ O.	Per cent. H.
0.0605	0.1945	87.66	0.0345	6.33

The simplest formula for this body would then be C₂₂H₁₁O.

In the third experiment of this series, the normal density was increased and also the quantity of sulphuric acid.

Experiment III.—

5 grams benzoïn.	N.D. ₁₀₀ = 4.5 amperes.
20 grams sulphuric acid (conc.).	Voltage = 6.5.
100 cc. alcohol.	Temperature, 75°.
	Time, 10 hours.

The current heat was sufficient to keep up the temperature. At the end of the time, adhering to the cathode and cell wall, was a yellow pasty mass which was detached, and on purification gave crystals similar in appearance to those obtained in Experiment II, and having the same melting-point, 205°–206°. The alcoholic filtrate yielded a small additional amount of the same body. As before the quantity of pure substance obtained was too small for a reliable analysis. The combustion gave the following:

Weight of substance in gram.	Weight of CO ₂ .	Per cent. C.	Weight of H ₂ O.	Per cent. H.
0.034	0.161	88.63	0.014	4.57

These results approximate the formula C₂₂H₁₁O.

*Reduction of Benzoin in Alcoholic Hydrochloric Acid Solution.**Experiment I.—*

2.5 grams benzoin.	N.D. ₁₀₀ = 4.5 amperes.
25 cc. hydrochloric acid (conc.).	Voltage = 7.
75 cc. alcohol.	Temperature, 75°.
	Time, 10 hours.

An anode of carbon was used in this as in the other experiments of this series. The current heat was sufficient to keep up the temperature.

When the cathode liquid cooled, a small amount of a yellow material deposited, which on purification by bone-black and boiling alcohol gave a white crystalline body having a melting-point of 205°–206°. The mother-liquor from these crystals, and that decanted from the cup in the first place, when combined and concentrated, gave a yellow paste which could not be crystallized, though portions of it were tried with the various solvents.

The quantity of pure material above, which melted at 205°–206°, was too small to make a trustworthy analysis. The combustion gave the following :

Weight of substance in gram.	Weight of CO ₂ .	Per cent. C.	Weight of H ₂ O.	Per cent. H.
0.0458	0.1451	86.39	0.623	5.58

This analysis approximates the formula C₁₁H₁₁O.

ELECTROLYTIC OXIDATION OF BENZIL.

The benzil used in the following experiments was prepared according to the method given in Gattermann's "Practical Methods of Organic Chemistry." Crude benzoin was finely pulverized and heated in an open flask with frequent shaking, with twice its weight of pure concentrated nitric acid, for two hours on a rapidly boiling water-bath. When the oxidation was ended the reaction mixture was poured into cold water; after the mass solidified the nitric acid was poured off; it was then washed several times with cold water, pressed out on a porous plate and crystallized from alcohol. After filtering off the separated crystals, they were dried in the air on several layers of filter-paper. The crystals melted at 94°.

The experiments in this series were carried out in a manner nearly analogous to those with benzoin.

*Oxidation of Benzil in Alcoholic Sodium Hydroxide Solution.**Experiment I.—*

2.5 grams benzil.	N.D. ₁₀₀ = 0.5 ampere.
5 grams sodium hydroxide.	Voltage = 9.
100 cc. alcohol.	Temperature, 40°–50°.
	Time, 10 hours.

The heat developed by the current was sufficient to hold the temperature between the above limits.

After neutralization of the alkali, evaporation of the alcohol and extraction with ether, nothing but a tarry mass was obtained, from which nothing definite could be isolated.

Experiment II.—

2.5 grams benzil.	N.D. ₁₀₀ = 1 ampere.
5 grams sodium hydroxide.	Voltage = 9–45.
100 cc. alcohol.	Temperature, 70°.
	Time, 6 hours.

The current kept the solution heated to 70°. The resistance of the solution increased so that at the end of six hours the current was stopped, the voltage having risen to forty-five.

The solution, treated as in Experiment I, yielded nothing but tarry products.

Experiment III.—

2.5 grams benzil.	N.D. ₁₀₀ = 0.5 ampere.
5 grams sodium hydroxide.	Voltage = 2.2.
75 cc. alcohol.	Temperature, 40°.
	Time, 6 hours.

A muslin bag was used instead of the porous cup for this experiment and a marked lowering of the resistance effected. The current heat alone raised the temperature to 40°.

The anode liquid yielded nothing but undecomposed benzil and tarry decomposition products as before.

*Oxidation of Benzil in Alcoholic Sulphuric Acid Solution.**Experiment I.—*

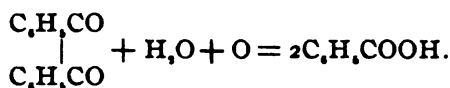
2.5 grams benzil.	N.D. ₁₀₀ = 3 amperes.
20 grams sulphuric acid (conc.).	Voltage = 6.5°.
100 cc. alcohol.	Temperature, 65°.
	Time, 10 hours.

The above temperature was maintained by the current heat alone.

When the alcohol was evaporated from the dark-colored anode liquid the odor of ethyl benzoate was observed. The ester was not separated, but the whole was shaken out with benzene and ligroin, the solvent removed and the residual liquid treated with an excess of sodium hydroxide and subjected to the heat of the water-bath for several hours. After the saponification of the ester, the liquid was acidified, shaken out with a mixture of ether and benzene and the solvent evaporated; the sublimation of the residue yielded crystals resembling benzoic acid, having a melting-point of 121° . A yield of eight and seven-tenths per cent. was obtained and the analysis gave the following:

Weight of substance in gram.	Weight of CO_2 .	Per cent. C.	Per cent. C calculated for $\text{C}_6\text{H}_5\text{COOH}$.
0.2442	0.6162	68.81	68.85
	Weight of H_2O .	Per cent. H.	Per cent. H calculated for $\text{C}_6\text{H}_5\text{COOH}$.
	0.1041	4.70	4.91

The reaction then proceeded according to the equation



Experiment II.—

2.5 grams benzil	N.D. ₁₀₀ = 1 ampere.
20 grams sulphuric acid (conc.).	Voltage = 10.5.
100 cc. alcohol.	Temperature, 65° .
	Time, 10 hours.

No outside heat was applied, the current alone raising the temperature to 65° at the end of one and one-half hours.

On subjecting the anode liquid to the same treatment as in Experiment I, a yield of 14.5 per cent. benzoic acid was obtained.

Oxidation of Benzil in Alcoholic Hydrochloric Acid Solution.

Experiment I.—

5 grams benzil.	N.D. ₁₀₀ = 1 ampere.
20 cc. hydrochloric acid (conc.).	Voltage = 3.
75 cc. alcohol.	Temperature, 60° .
	Time, 10 hours.

Nothing but benzil separated when the cup contents cooled, and the alcoholic filtrate contained benzil and a small amount of tarry substance.

For the next experiment the normal density was increased to seven amperes.

Experiment II.—

5 grams benzil	N.D. ₁₀₀ = 7 amperes.
25 cc. hydrochloric acid (conc.).	Voltage = 6.
100 cc. alcohol.	Temperature, 70°–75°.
	Time, 9 hours.

Here again a crystalline mass of benzil separated when the anode liquid cooled. The alcoholic filtrate contained nothing but benzil and some tarry decomposition products.

ELECTROLYTIC REDUCTION OF BENZIL.

Reduction in Alcoholic Sodium Hydroxide Solution.

Experiment I.—

2.5 grams benzil.	N.D. ₁₀₀ = 0.5 ampere.
5 grams sodium hydroxide.	Voltage = 3.3.
100 cc. alcohol.	Temperature, 30°
	Time, 6 hours.

A muslin bag was used for the porous septum in this experiment. The current kept the temperature at 30°.

The cathode liquor was neutralized with hydrochloric acid and the alcohol removed by evaporation. The residual liquid on cooling deposited a small amount of a white crystalline material, together with the unchanged benzil, which collected in a lump. The white crystals were readily soluble in cold alcohol and to a less degree in hot water. After a crystallization from hot water the crystals melted with some decomposition at 145°–146°. Not a sufficient quantity of this body was obtained for a combustion.

Experiment II.—

2.5 grams benzil.	N.D. ₁₀₀ = 3 amperes.
5 grams sodium hydroxide.	Voltage = 5.
100 cc. alcohol.	Temperature, 50°.
	Time, 6½ hours.

The current heat held the temperature at 50°. After neutralization with hydrochloric acid and removal of the alcohol, a small amount of white needle-like crystals separated, together with benzil and some tarry matter. The crystals were separated, dissolved in hot water, treated with bone-black, and recrystallized.

The body had no definite melting-point, beginning to fuse and decompose at 185° .

Reduction of Benzil in Alcoholic Sulphuric Acid Solution.

Experiment I.—

2.5 grams benzil.	N.D. ₁₀₀ = 4 amperes.
20 grams sulphuric acid (conc.).	Voltage = 9.
100 cc. alcohol.	Temperature, 65° .
	Time, $15\frac{1}{2}$ hours.

No outside heat was applied, the current holding the temperature at 65° . On standing over night a small amount of a white crystalline substance separated, which was removed and purified, giving a melting-point of 205° – 206° . The removal of the alcohol caused the deposition in small amount of a yellow, pasty mass, which oxidized very readily and could not be crystallized.

The white crystalline body above is probably the same as that obtained in several previous reductions. So little of these substances melting at 205° – 206° was obtained in the various reductions that the analytical results have little value in establishing their identity, although the physical properties are the same. The white body obtained in this reduction analyzed as follows, approximating the formula $C_{14}H_{12}O$:

Weight of substance in gram.	Weight CO_2 .	Per cent. C.	Weight H_2O .	Per cent. H.
0.048	0.161	91.46	0.0215	4.97

Experiment II.—

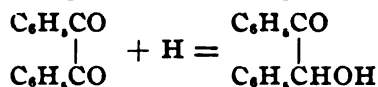
2.5 grams benzil.	N.D. ₁₀₀ = 1 ampere.
20 grams sulphuric acid (conc.).	Voltage = 4.
100 cc. alcohol.	Temperature, 40° .
	Time, $10\frac{1}{2}$ hours.

The current heat alone kept up the temperature. When the current was interrupted it was found that a mass of white crystals lined the walls of the porous cup and adhered to the cathode. The crystals were washed with water, dissolved in alcohol, treated with bone-black and crystallized, melting sharply at 134° . When sublimed, these crystals suffered decomposition. In physical properties the body resembled benzoin and the analysis confirms this:

Weight of substance in gram.	Weight of CO_2 .	Per cent. C.	Per cent. C calculated for benzoin $C_{14}H_{12}O_2$.
0.189	0.5495	79.28	79.24

Weight of H ₂ O.	Per cent. H.	Per cent. H calculated for benzoin C ₁₄ H ₁₂ O ₂ .
0.0985	5.78	5.66

The reaction then proceeds according to the equation:



The yield of benzoïn obtained was 31 per cent.

Reduction of Benzil in Alcoholic Hydrochloric Acid Solution.

Experiment I.—

5 grams benzil.	N.D. ₁₀₀ = 1 ampere.
20 cc. hydrochloric acid (conc.).	Voltage = 2.2.
150 cc. alcohol.	Temperature, 30°.
	Time, 10 hours.

No external heat was applied. As with the sulphuric acid solution, there were white crystals hanging in masses to the cathode and the walls of the porous cup. These crystals were purified as in the above experiment and melted sharply at 134°. The alcoholic filtrate yielded more of the benzoïn, making a total yield of 39 per cent. The analysis gave the following:

Weight of substance in gram.	Weight of CO ₂ .	Per cent. C.	Per cent. C calculated for benzoin C ₁₄ H ₁₂ O ₂ .
0.206	0.6075	80.42	79.24
	Weight of H ₂ O.	Per cent. H.	Per cent. H calculated for benzoin C ₁₄ H ₁₂ O ₂ .
	0.105	5.66	5.66

SUMMARY.

Comparison of the Above Results with those Obtained by the Usual Oxidizing and Reducing Agents.

Benzoin, when treated with chromic acid, yields benzaldehyde and benzoic acid, while Fehling's solution, nitric acid, or chlorine oxidizes it to benzil.

The electrolytic oxidation in sodium hydroxide solution with normal density of 0.25 ampere gave the maximum yield of benzoic acid, while higher densities gave less acid and larger quantities of tarry decomposition products. With sulphuric acid solution the normal density had to be raised five-tenths ampere in order to effect oxidation, yet an increase in density here, as with the sodium hydroxide solution, gave more tarry matter and less benzoic acid.

In hydrochloric acid solution the experiment with normal density at one ampere gave as oxidation products both benzoic acid and benzil, while densities above this gave large yields of benzil alone, and an increase in both time and density factors gave only tarry decomposition products.

Sodium amalgam or benzoïn yields hydrobenzoïn together with a little isohydrobenzoïn. Zinc and hydrochloric acid reduction of benzoïn yields desoxybenzoïn.

The experiments on the electrolytic reduction of benzoïn gave as the only definite product the body melting at 205° – 206° , which was obtained both in hydrochloric and sulphuric acid solutions.

The ordinary chromic acid oxidation of benzil yields benzoic acid.

With sodium hydroxide solution and densities of five-tenths and one ampere the electrolytic oxidation of benzil gave no definite products even when, as in one case, some benzil remained in the cup unchanged.

In sulphuric acid solution the electrolytic oxidation of benzil gave benzoic acid, 14.5 per cent. being the highest amount obtained.

With electrolytic oxygen in hydrochloric acid solution, benzil was unchanged when the normal density was equal to one ampere and an increase to seven amperes gave only a partial decomposition and indefinite tarry substances.

Benzil reduced by zinc and hydrochloric acid gives benzoïn or desoxybenzoïn according to the conditions.

The electrolytic reduction of benzil in sodium hydroxide solution gave nothing definite.

In sulphuric acid solution, benzil gave by the current reduction benzoïn, the product crystallizing in an almost pure condition on the walls of the porous cup. An increase in the time factor gave besides decomposition products, a small amount of the body melting at 205° – 206° , which is evidently the same as that obtained in the reduction of benzoïn in both sulphuric and hydrochloric acid solutions.

By the current reduction in hydrochloric acid solution benzil gave benzoïn in a crystalline form that was almost pure when taken from the cup.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 43.]

ELECTROLYTIC DETERMINATIONS AND SEPARATIONS.

By LILY G. KOLLOCK.¹

Received July 14, 1899.

INTRODUCTION.

THAT the electric current has greatly aided in the development of new and reliable methods for the determination and separation of metals is no longer questioned. That new material will continue to be added to what we now possess is also certain to occur. But in the old methods, worked out long before correct ideas prevailed as to current density, concentration of the solution and electrode surface, gaps exist, and uncertainty must necessarily prevail in the minds of those who seek to reproduce the proper working conditions of these earlier methods. That the latter are in every sense satisfactory in the hands of those persons who are thoroughly acquainted with them is also beyond question. To render them, however, universally acceptable, and to render their place in analytical chemistry by electrolysis permanent, the absolute conditions for successful work on the part of any investigator, must be definitely established. To this end a number of the earlier methods in which the double cyanides were used as electrolytes have been carefully reviewed in the following pages, and the conditions of current density, amperage, voltage, and other factors fully worked out. Thus edited, doubt can no longer be thrown upon the methods proposed, and they will continue to be in their developed condition the most reliable for the purposes for which they have been suggested. They now for accuracy, neatness, and rapidity of execution most certainly excel the ordinary gravimetric and volumetric methods applied to the same metals.

CADMIUM.

In 1878 Smith showed that cadmium could be precipitated quantitatively from its alkaline double cyanide solution. In the following experiments cadmium sulphate containing 0.1659 gram cadmium in ten cc. was converted into the double cyanide, using

¹ From author's thesis for the degree of Ph.D.

one gram of potassium cyanide. The solution was electrolyzed with a current $N.D._{100} = 0.04-0.06$ A and $V = 2.9-3.2$. The solution was heated to 60° C. After the current had passed for six hours, the deposit was washed with hot water and alcohol, dried and then weighed. The solution poured out of the platinum dish, and examined qualitatively for cadmium, showed that all the cadmium had been deposited in this time. It was likewise entirely precipitated when the current was allowed to act on the solution through the night in the cold. The following results were obtained :

RESULTS.

Cad- mium. Gram.	Potassium cyanide. Gram.	Di- lution. cc.	Current.	Volt- age.	Tem- pera- ture.	Time.	Metal found. Gram.
0.1659	1	125	$N.D._{100} = 0.06$ A.	2.9	57°	7 hours	0.1657
0.1659	1	125	$N.D._{100} = 0.04$ A.	2.9	cold	during night	0.1650
0.1659	1	125	$N.D._{100} = 0.06$ A.	3.2	60°	3 hours	0.1655

SILVER.

It is stated¹ that silver may be precipitated from a cyanide solution containing an excess of potassium cyanide. It may be deposited with a low current, and has the advantage of non-precipitation of silver peroxide at the anode.

Accordingly a silver nitrate solution containing 0.1270 gram of silver in 25 cc., after the addition of 0.5 gram of potassium cyanide, was diluted to 125 cc. This solution was electrolyzed with a current $N.D._{100} = 0.07$ A and $V = 3.2$. The temperature was 65° C. The deposition was complete in three hours. With a current of $N.D._{100} = 0.1$ A the silver was deposited completely in two hours. The relation between the current and the time factor may be seen in the following table :

RESULTS.

Silver. present. Gram.	Potassium cyanide. Gram.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Found. Gram.
0.1270	0.5	100	$N.D._{100} = 0.07$ A.	3.2	65°	3	0.1271
0.1270	0.5	100	$N.D._{100} = 0.07$ A.	3.2	65°	3	0.1270
0.1270	0.5	100	$N.D._{100} = 0.06$ A.	3.2	65°	3	0.1273
0.1270	1	100	$N.D._{100} = 0.01$ A.	3	65°	2	0.1268
0.1026	1	100	$N.D._{100} = 0.04$ A.	2.5	65°	5	0.1026
0.1026	1	100	$N.D._{100} = 0.04$ A.	2.5	65°	5	0.1024

¹ Smith's Electro-Chemical Analysis, p. 77.

SEPARATIONS.

Silver from Platinum.—Smith¹ described this separation. A current of one cc. of oxy-hydrogen gas per minute acted upon a solution of the double cyanide produced by adding two and five-tenths grams of potassium cyanide. The silver was deposited free from any trace of platinum.

The separation, therefore, was taken up in order to get the exact working conditions. The salts of the metals used were silver nitrate containing 0.1026 gram of silver, and platinum chloride containing from 0.0879 gram to 0.1758 gram of platinum. To the combined solutions 1.25 grams of potassium cyanide were added and the whole diluted to 125 cc. The current used was $N.D._{100} = 0.04$ A and $V = 2.5$. The temperature was 70° . In from three to four hours the current was interrupted and the deposit washed with hot water and alcohol. It was found to be free from platinum. The filtrate gave no reaction for silver.

RESULTS.

Silver. Gram.	Plati- num. Gram.	Potassium cyanide. Gram.	Current.	Volt- age.	Tem- pera- ture.	Dilu- tion. cc.	Time. Hours.	Found. Gram.
0.1026	0.879	0.5	$N.D._{100} = 0.05$ A.	2.5	78°	125	5	0.1030
0.1026	0.1758	1.25	$N.D._{100} = 0.05$ A.	2.5	75°	125	3	0.1022
0.1026	0.1758	1.25	$N.D._{100} = 0.45$ A.	2.4	75°	125	3	0.1028
0.1026	0.1758	1.25	$N.D._{100} = 0.04$ A.	2.5	75°	125	3	0.1025
0.1026	0.1758	1.25	$N.D._{100} = 0.04$ A.	2.5	75°	125	3	0.1025

Silver from Copper.—In the *American Chemical Journal*,¹ there appears a series of forty experiments relating to the separation of these metals. Copper was found to have been precipitated with the silver when the deposition took place from a cyanide solution. It was then thought that copper could not be separated from silver by this method. In 1889 a set of new experiments was reported. By lowering the strength of the current the separation was made. The silver deposit contained no copper nor could silver be detected in the copper solution poured from the dish. In 1895 Smith and Wallace published a report of the separation made in that year.

I found that the following conditions gave accurate results. The solution of silver nitrate used contained 0.1024 gram of

¹ *Am. Chem. J.*, 13, 417.

² *Ibid.*, 11, 264.

metal and that of copper nitrate contained 0.0998 gram of copper. To the mixed solution two grams of potassium cyanide were added. The liquid containing an excess of potassium cyanide was diluted to 125 cc. This was subjected to a current of $N.D._{100} = 0.03-0.05$ A and $V = 1.1-1.66$. The current acted from three to seven hours. The deposit of silver was free from copper.

The results varied from the theoretical by 0.0002-0.0003 gram.

RESULTS.

Silver. Gram.	Copper. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Found. Gram.
0.1024	0.0998	2	125	$N.D._{100} = 0.03$ A.	1.16	cold	10	0.1027
0.1024	0.1	2	125	$N.D._{100} = 0.05$ A.	1.1	65°	7	0.1026
0.1024	0.1	1	125	$N.D._{100} = 0.058$ A.	1.66	65°	3	0.1026

Silver from Cadmium.—Smith and Spencer¹ found that the deposition of silver was accelerated by heating the solution during the electrolysis, and that while cadmium may be entirely precipitated in the cold by the current, yet with a low current and a temperature of 60° the cadmium is held in solution. A separation of silver and mercury may thus be effected in a cyanide solution. In the same journal, Smith and Frankel record the separation of mercury from cadmium, zinc, nickel, and cobalt. In 1895 Smith and Wallace published later results with the same method. Following the data thus obtained, a solution of silver nitrate containing 0.1024 gram of silver and cadmium sulphate solution equivalent to 0.168 gram of cadmium was used. The salts were transformed into their double cyanides by an excess of potassium cyanide. The silver was obtained free from cadmium in four hours. The current used was $N.D._{100} = 0.02$ A and $V = 2.15$. The temperature was 60° before the current was passed through the solution.

RESULTS.

Silver. Gram.	Cad- mium. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Found. Gram.
0.1024	0.168	2	125	$N.D._{100} = 0.02$ A.	2.15	75°	4	0.1025
0.1024	0.168	2	125	$N.D._{100} = 0.02$ A.	2.1	60°	4	0.1020
0.1024	0.168	2	125	$N.D._{100} = 0.025$ A.	2.15	65°	5	0.1027

The silver in all cases was found free from cadmium.

¹ This Journal, 16, 420.

Silver from Zinc.—These metals were separated according to the following conditions: Using zinc sulphate containing one-tenth gram of zinc and silver nitrate solution containing 0.1024 gram of silver. The potassium cyanide used amounted to one gram. The solution was 125 cc. in volume. It was electrolyzed at 70° by a current of $N.D._{100} = 0.032-0.038$ A and $V = 2.76$. In three hours the deposition of the silver was complete.

RESULTS.

Silver. Gram.	Zinc. Gram.	Potassium cyanide. Gram.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Found. Gram.
0.1024	0.1	1	100	$N.D._{100} = 0.33$ A.	2.76	60°	3	0.1026
0.1024	0.1	1	100	$N.D._{100} = 0.38$ A.	2.73	70°	3	0.1028
0.1024	0.1	1	100	$N.D._{100} = 0.38$ A.	2.70	65°	3	0.1027

Nickel and cobalt were separated from silver in a similar way.

Silver from Nickel.—A solution of nickel nitrate containing one-tenth gram of nickel was added to a silver nitrate solution and both converted into the double cyanides by one and five-tenths grams of potassium cyanide. The solution was electrolyzed with a current $N.D._{100} = 0.02-0.03$ A and $V = 1.7-2$ for three hours. The separation in this time was found to be complete. The results show a variation from the calculated amount of $+0.0001$ gram to -0.0002 gram. The solution of silver in nitric acid, when examined qualitatively, gave no evidence of the presence of nickel. The nickel solution, when examined, showed that the silver had been entirely precipitated.

RESULTS.

Silver. Gram.	Nickel. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Found. Gram.
0.1024	0.1	1.5	125	$N.D._{100} = 0.02$ A.	1.7	65°	3	0.1026
0.1024	0.1	1.5	125	$N.D._{100} = 0.03$ A.	2.	65°	5	0.1025
0.1024	0.1	1.5	125	$N.D._{100} = 0.03$ A.	1.66	60°	3	0.1025

Silver from Cobalt.—Cobalt nitrate was the salt used in this separation. To the solution of silver nitrate (0.1024 gram of silver) was added a solution of the cobalt salt containing 0.1 gram of cobalt and 2.75 grams of potassium cyanide. A current of $N.D._{100} = 0.02$ A and $V = 2.2-2.7$ at a temperature of 65° was passed through the solution for five hours. The silver in this time was entirely precipitated. No cobalt was found deposited with the silver.

RESULTS.

Silver. Gram.	Co- balt. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Found. Gram.
0.1024	0.1	2.75	125	N.D. ₁₀₀ =0.038 A.	2.2	65°	5	0.1028
0.1024	0.1	3.5	125	N.D. ₁₀₀ =0.02 A.	2.2	65°	3½	0.1027

Silver from Iron.—Heretofore these metals have not been separated electrolytically in cyanide solution. A solution of ferrous ammonium sulphate, equivalent to one-tenth gram of metallic iron, was treated with sulphurous acid in order to reduce any ferric iron which might exist. After the reduction was complete the excess of acid was nearly neutralized with potassium carbonate; to this two and five-tenths grams of potassium cyanide were added. The solution of the double cyanide, dark green in color, was added to a solution of silver which had been converted into the double cyanide by five-tenths gram of potassium cyanide. The entire solution was made up to 100 cc. It was heated to 65° and electrolyzed with a current of N.D.₁₀₀ = 0.04 A and V = 2.7. At the expiration of three hours the silver was found to be entirely deposited. There was in some cases a separation of ferric oxide at the anode. The silver, after its solution in nitric acid, was tested for iron by ammonium thiocyanate. A faint pink color, due to a trace of iron in the acid used for the solution of the metal, was observed. The deposit, which was light gray in color, varied but slightly from the theoretical amount of the silver present in the solution.

RESULTS.

Silver. Gram.	Iron. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Found. Gram.
0.1002	0.1	3	125	N.D. ₁₀₀ =0.025 A.	1.8	65°	4	0.1001
0.1002	0.1	2.5	125	N.D. ₁₀₀ =0.02 A.	1.8	70°	4	0.1005
0.1002	0.1	3.25	125	N.D. ₁₀₀ =0.038 A.	2.2	65°	3	0.1000
0.1174	0.1	3	125	N.D. ₁₀₀ =0.04 A.	2.25	70°	3	0.1176
0.1174	0.2	4	125	N.D. ₁₀₀ =0.04 A.	2.2	70°	3	0.1174
0.1174	0.1	3	125	N.D. ₁₀₀ =0.05 A.	2.2	75°	3	0.1175

MERCURY.

It is recorded¹ that mercury may be separated without difficulty with a low current and a large excess of alkaline cyanide. The deposits are noted as "compact, rather gray in color, and

¹ *Am. Chem. J.*, 11, 264.

showed in a few cases a drop-like nature so characteristic of mercury.' The time required for the deposition under the conditions given was twelve to fourteen hours. Smith and Wallace,¹ published a number of separations of mercury from other metals—zinc, cadmium, cobalt, and nickel. The time required for separation was reduced to three and three and one-half hours.

In the experiments made this year the following conditions gave good results and confirmed those previously made. A solution of mercuric chloride, containing 0.1439 gram of mercury in ten cc. and five-tenths gram of potassium cyanide, was diluted to 100 cc. It was electrolyzed with a current $N.D._{100} = 0.07$ A and $V = 3.2$. The temperature of the solution was 65° C. In three hours the metal was completely deposited. The deposit was washed with slightly warm water.

RESULTS.

Mer- cury. Gram.	Potassium cyanide. Gram.	Dilution. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Merc'y found. Gram.
0.1439	0.5	100	$N.D._{100} = 0.07$ A.	3.2	65°	$3\frac{1}{2}$	0.1441
0.1439	0.5	100	$N.D._{100} = 0.07$ A.	3.2	65°	$3\frac{1}{2}$	0.1442
0.1439	0.5	100	$N.D._{100} = 0.02$ A.	1.6	65°	6	0.1440
0.1439	0.5	100	$N.D._{100} = 0.07$ A.	3.1	65°	3	0.1436

The deposits obtained were light gray in color and were easily washed. They were bright and metallic in appearance, with higher voltage.

SEPARATIONS.

Mercury from Copper.—Smith and Frankel² report the separation of mercury and copper in an alkaline cyanide solution. A current generating two cc. of oxyhydrogen gas per minute was used for this purpose. The solution used contained 0.1833 gram of mercury and 14–70 per cent. of copper were added. With a current generating three and two-tenths cc. of oxyhydrogen gas, mercury was completely deposited in sixteen hours. It is stated, however, that when the quantity of copper present exceeded twenty per cent. the results were unsatisfactory. Later Smith and McCauley took up the separation again and by careful regulation of the current, were enabled to effect it even when the metals were present in equal quantities.

¹ This Journal, 17, 612.

² Am. Chem. J., 11, 264.

In repeating this work a solution of mercuric chloride equivalent to 0.1216 gram of mercury and a copper sulphate solution, equivalent to one-tenth gram of copper were used. An excess of potassium cyanide was added. The entire solution was diluted to 125 cc. The current acting upon the solution was $N.D._{100} = 0.04$ A and $V = 1.09$. The temperature was 65° . In from two to four hours the mercury was completely deposited. On testing the metal qualitatively, the deposit was found free from copper.

RESULTS.

Mer- cury. Gram.	Cop- per. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Temper- ature.	Time. Hours.	Mer'cy found. Gram.
0.1216	0.1	2.0	125	$N.D._{100} = 0.02$ A.	1.09	cold	16	0.1220
0.1216	0.1	2.5	125	$N.D._{100} = 0.03$ A.	1.9	65°	4	0.1216
0.1216	0.15	3.5	125	$N.D._{100} = 0.035$ A.	1.8	65°	2½	0.1213
0.1216	0.1	3.0	125	$N.D._{100} = 0.04$ A.	1.9	65°	3	0.1215

Mercury from Nickel.—These metals were separated in an analogous manner to that described under the separation of silver from nickel. To the solutions of mercuric chloride and nickel nitrate were added two grams of potassium cyanide. This was then diluted to 125 cc. A current of $N.D._{100} = 0.04$ A and $V = 2.2$ was allowed to act for three hours. The deposit was found to weigh 0.0003 gram less than the calculated amount of mercury present. The filtrate was found to contain no mercury. No nickel was deposited with the metal.

RESULTS.

Mer- cury. Gram.	Nickel. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Temper- ature.	Time. Hours.	Mer'cy found. Gram.
0.1216	0.1	2	125	$N.D._{100} = 0.04$ A.	1.7	65°	4	0.1220
0.1216	0.1	2	125	$N.D._{100} = 0.04$ A.	2.2	65°	4	0.1220
0.1216	0.15	2.5	125	$N.D._{100} = 0.04$ A.	2.2	65°	4	0.1211
0.1216	1	2	125	$N.D._{100} = 0.04$ A.	2.2	65°	4	0.1213

Mercury from Cobalt.—The mercuric chloride used in this separation contained 0.1216 gram of mercury and the cobalt nitrate contained one-tenth gram of cobalt. Two grams of potassium cyanide were added to the mixed solutions which were diluted to 100 cc. The current acting was $N.D._{100} = 0.03$ A and $V = 2.9$. With a temperature of 60° the deposition of the mercury was complete in five hours. It was free from cobalt.

RESULTS.

Mer- cury. Gram.	Co- balt. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Merc'y depos- ited. Gram.
0.1216	0.1	2	100	N.D. ₁₀₀ =0.025 A.	2.45	cold	16	0.1217
0.1216	0.1	2	100	N.D. ₁₀₀ =0.025 A.	2.06	65°	5	0.1213
0.1158	0.1	2	100	N.D. ₁₀₀ =0.03 A.	2.9	65°	5	0.1152

Mercury from Zinc.—The results obtained in the separation of mercury from zinc were first reported by Smith and Frankel in 1889. The electrolysis took place at the ordinary temperature in sixteen hours, with a current generating three cc. of oxyhydrogen gas per minute.

In the experiments made this year the following conditions gave satisfactory results.

RESULTS.

Mer- cury. Gram.	Zinc. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Found. Gram.
0.1158	0.1	2	125	N.D. ₁₀₀ =0.05 A.	3	60°	4	0.1152
0.1158	0.1	1.5	125	N.D. ₁₀₀ =0.033 A.	2.5	50°	4	0.1155
0.1158	0.2	2	125	N.D. ₁₀₀ =0.025 A.	2.9	50°	4	0.1155

In the third determination the current acted for three hours at 50°, and then all night in the cold. The deposit in all cases was gray and compact. The mercury on examination for zinc gave no reaction for that metal, while no mercury was found in the zinc solution.

Mercury from Cadmium.—As stated under the separation of silver from cadmium, Smith and Wallace¹ found that cadmium might be separated from both silver and mercury by keeping the temperature slightly elevated. Unless this precaution is taken cadmium is precipitated with both metals, even when a low current is used.

The following proved to be good working conditions: The mercuric chloride solution used contained 0.1182 gram of mercury, and the cadmium sulphate solution was equivalent to 0.2206 gram of cadmium. The double alkaline cyanides were produced by the addition of two and one-half grams of potassium cyanide. A current of N.D.₁₀₀=0.018 A and V=1.7 was passed through the solution, previously heated to 65° for seven hours. The mercury deposit was free from cadmium and weighed 0.1181 gram, which was 0.0001 gram lighter than the

¹ This Journal, 17, 612.

theoretical amount of mercury. It was repeatedly found that when the current was greater than 0.02 A, cadmium was precipitated.

Mercury from Platinum.—This separation was first carried out and reported by Smith.¹ The deposit of mercury was effected by using a current generating two cc. of oxyhydrogen gas a minute. The alkaline cyanide used for 0.1902 gram of mercury was two and a half grams. According to these suggestions a separation of the two metals was made. The mercury in solution was 0.1373 gram, and the platinum in the platinic chloride contained from 0.025 gram to 0.1 gram. In four hours the separation was completed. The current was $N.D._{100} = 0.05$ A and $V = 2.1-2.3$. The results show an error of -0.0001 gram to $+0.0003$ gram.

RESULTS.

Mer- cury Gram.	Plat- inum. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Merc'y depos- ited. Gram.
0.1373	0.025	3	125	$N.D._{100} = 0.05$ A.	2.12	65°	4	0.1372
0.1373	0.01	3	125	$N.D._{100} = 0.04$ A.	2.12	75°	4	0.1376
0.1373	0.01	3	125	$N.D._{100} = 0.045$ A.	2.12	70°	4	0.1375

Mercury from Iron.—The separation of mercury from iron, like that of silver from iron, has not been previously attempted in alkaline cyanide solution. Accordingly the following method was developed and found to yield satisfactory results:

The solution of the cyanide of iron was prepared from ferrous ammonium sulphate in precisely the same way as that described in the separation of silver from iron. The mercuric chloride solution contained 0.1216 gram of mercury. The cyanide present was from one to three grams, and the current was $N.D._{100} = 0.05$ A and $V = 2.5$. The temperature during the electrolysis was maintained at 70° C. In three hours the mercury was completely deposited. It was free from iron. The mercury deposit was dissolved in concentrated nitric acid. After diluting, a few crystals of ammonium thiocyanate were added. A faint pink color was observed, which was found to be due to the small trace of iron in the nitric acid.

¹ *Am. Chem. J.*, 13, 417.

RESULTS.

Mer- cury. Gram.	Iron. Grams.	Potassium. cyanide. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Mer- cury depos- ited. Gram.
0.1216	0.1	1	100	N.D. ₁₀₀ =0.05 A.	2.	70°	3	0.1215
0.1216	0.3	3	100	N.D. ₁₀₀ =0.04 A.	2.	70°	4	0.1217
0.1216	2.5	2.5	100	N.D. ₁₀₀ =0.02 A.	2.7	65°	4	0.1217

GOLD SEPARATIONS.

Smith and Muhr¹ report the separation of gold from palladium, platinum, zinc, cobalt, nickel, and copper.

Gold from Palladium.—It has been previously shown that palladium is not deposited with a current of 0.01 A in the presence of an excess of potassium cyanide. With a current liberating eight-tenths cc. of oxyhydrogen gas a minute, and the solution containing one and five-tenths grams of potassium cyanide, 0.1162 gram of gold was deposited in from twelve to fourteen hours.

In accordance with this suggestion, the following conditions were obtained: Two grams of potassium cyanide were added to a solution of gold chloride containing 0.1256 gram of metal and palladium chloride equivalent to one-tenth gram of metallic palladium. This was diluted to 250 cc. The current used was N.D.₁₀₀=0.06–0.09 A and $V=1.5$. The temperature during the decomposition was 65°. In five hours the current was raised to 0.09 A. The gold was found to be completely deposited and free from palladium.

RESULTS.

Gold. Gram.	Palla- dium. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Gold found. Gram.
0.1256	0.1	2	125	N.D. ₁₀₀ =0.06–0.03 A.	2.5	65°	6	0.1250
0.1256	0.1	2	250	N.D. ₁₇₅ =0.06–0.09 A.	2.5	65°	6	0.1257

Gold from Copper.—In the report referred to, the separation of gold from copper in cyanide solution took place with a current liberating eight-tenths cc. of oxyhydrogen gas at the ordinary temperature in about twelve hours.

It was found that by heating the solution to 65° the precipitation was more rapid, but required more cyanide in order to keep the copper from being deposited with the gold. To a solution of gold chloride containing 0.1665 gram of metallic gold and cop-

¹ *Am. Chem. J.*, 13, 417.

per sulphate containing one-tenth gram of copper, were added four grams of potassium cyanide. The solution (250 cc.), warmed to 65° , was electrolyzed with a current of $N.D._{100} = 0.05-0.07$ A and $V = 1.7$ for two and one-half hours. In this time 0.1667 gram of gold was obtained. There was no reaction for copper when the deposit treated with nitric acid was tested for that metal.

RESULTS.

Gold. Gram.	Cop- per. Gram.	Potassium cyanide. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Gold found. Gram.
0.1665	1	2	250	$N.D._{175} = 0.07$ A.	1.7	65°	$2\frac{1}{2}$	0.1667
0.1627	1	2	250	$N.D._{175} = 0.05-0.08$ A.	1.9	65°	3	0.1627

Gold from Nickel.—The conditions under which this separation is made are similar to those obtained *under* the separations of silver and mercury from nickel. The solution of gold chloride used was equivalent to 0.1610 gram of metallic gold, and nickel nitrate contained one-tenth gram of nickel. They were converted into their double cyanides by the addition of four grams of potassium cyanide. A current of $N.D._{100} = 0.05$ A and $V = 1.5$ was passed through the solution (125 cc.) at 60° for six hours. The gold on examination contained no nickel.

RESULTS.

Gold. Gram.	Nickel. Gram.	Cya- nide. Grams.	Dilu- tion. cc.	Current.	Voltage.	Tem- pera- ture.	Time. Hours.	Gold found. Gram.
0.1567	0.1	4	125	$N.D._{100} = 0.05$ A.	1.7	65°	7	0.1567
0.1610	0.1	4	125	$N.D._{100} = 0.05$ A.	1.5	60°	7	0.1603

Gold from Cobalt.—More difficulty was experienced with the separation of these metals than with the preceding. Four grams of potassium cyanide were added to the solution of gold chloride and cobalt nitrate equivalent to one-tenth gram of cobalt. The current used for the deposition of the gold was $N.D._{100} = 0.05$ A and $V = 1.7$. The electrolysis was carried out at 60° C. It was found advantageous before the end to add one cc. of a twenty percent. sodium hydroxide solution, and raise the current to 0.08 A, in order to deposit the last trace of gold. In this way the gold was entirely deposited in seven hours free from cobalt.

RESULTS.

Gold. Gram.	Cobalt. Gram.	Cyanide. Grams.	Dilution. cc.	Current.	Voltage.	Temperature.	Dilution. cc.	Time. Hours.	Gold found. Gram.
0.1610	0.1	4	125	N.D. ₁₀₀ = 0.05-0.08 A.	1.7	60°	125	6½	0.1612
0.1610	0.1	4	125	N.D. ₁₀₀ = 0.05-0.08 A.	1.7	60°	125	6	0.1608
0.1495	0.1	4	250	N.D. ₁₇₅ = 0.05-0.08	1.7-2	60°	250	6	0.1497

Gold from Zinc.—These metals were successfully separated according to the following conditions: Four grams of potassium cyanide were added to a solution of gold chloride and zinc sulphate containing one-tenth gram of zinc. The current acting upon the double cyanides was $N.D._{100} = 0.06$ A and $V = 2.66$. The temperature of the solution was 60°. In seven hours the deposition was complete. No zinc was found with the gold.

RESULTS.

Gold. Gram.	Zinc. Gram.	Cyanide. Grams.	Current.	Voltage.	Dilution. cc.	Temperature.	Time. Hours.	Gold found. Gram.
0.1495	0.1	4	N.D. ₁₀₀ = 0.06 A.	2.66	125	60°	7	0.1490
0.1608	1.	4	N.D. ₁₇₅ = 0.06 A.	2.7	250	65°	7	0.1602

Gold from Platinum.—To the solution of gold chloride containing 0.1576 gram of gold and platinic chloride equivalent to 0.125 gram of platinum, were added one and five-tenths grams of potassium cyanide. The volume of the solution was 250 cc. A current of $N.D._{175} = 0.01$ A and $V = 2.7$ was used. The temperature was 70° C. In three hours the gold was entirely precipitated. No platinum was deposited with the gold. The deposit weighed 0.1479 gram.

Mercury from an Alkaline Sulphide Solution.—In 1891 Smith made the statement that mercury obtained as mercuric sulphide, during analysis may be accurately estimated electrolytically. The sulphide was dissolved in sodium sulphide of sp. gr. 1.19, and electrolyzed with a current generating one cc. of oxyhydrogen gas per minute, acting during the night. The mercury was always compact and gray in color.

In working out conditions for the determination of mercury by this method, twenty-five cc. of sodium sulphide were added to a solution of mercuric chloride containing 0.1403 gram of mercury. This solution, diluted to 125 cc., was electrolyzed at 70° C. by a current of $N.D._{100} = 0.11$ A and $V = 2.5$. In five hours the mercury was entirely deposited. It was light gray in

color. Slightly warm water was used in washing the deposit.

RESULTS.

Mer- cury. Gram.	Sodium sulphide, sp. gr. 1.19. cc.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Mercury found. Gram.	Error. Gram.
0.1403	25	100	N.D. ₁₀₀ = 0.11 A.	2.5	70°	5	0.1400	0.0003
0.1403	25	100	N.D. ₁₀₀ = 0.12 A.	2.7	70°	5	0.1404	0.0001

COPPER.

"Moore advises dissolving the recently precipitated copper sulphide obtained during the ordinary course of analysis in potassium cyanide, and after the addition of an excess of ammonium carbonate, electrolyze the warm (70°) solution." According to this suggestion the following conditions for the determination of copper were found to give good results: The copper sulphate solution used contained 0.1270 gram of metallic copper. This was precipitated as sulphide, which was dissolved in two grams of potassium cyanide and ammonium carbonate added. The solution, diluted to 125 cc., was heated to 70° C. and electrolyzed with a current of N.D.₁₀₀ = 0.02–0.07 A and $V = 4$. In three hours the copper was completely deposited. The copper was found to weigh 0.1269 gram, that is 0.0001 gram less than the theoretical amount.

Copper from Nitric Acid Solution.—Copper has also been successfully determined electrolytically in a nitric acid solution.* A solution containing ten cc. of concentrated nitric acid was diluted to 100 cc. and electrolyzed. The current used was N.D.₁₀₀ = 0.03 A and $V = 1.7$. At the ordinary temperature in sixteen hours 0.1396 gram of copper was precipitated. The solution treated with ammonium hydroxide showed that the copper had been entirely deposited. With a temperature of 65° and a current of N.D.₁₀₀ = 0.09 A and $V = 1.9$ in five hours 0.1397 gram of copper was found, and another determination under identical conditions gave the theoretical amount of copper present.

RESULTS.

Copper. Gram.	Nitric acid. cc.	Dilution. cc.	Current.	Volt- age.	Temper- ature.	Time. Hours.	Copper found. Gram.
0.1398	10	100	N.D. ₁₀₀ = 0.03 A.	1.7	cold	16	0.1396
0.1398	10	100	N.D. ₁₀₀ = 0.09 A.	1.9	70°	16	0.1397
0.1398	10	100	N.D. ₁₀₀ = 0.09	1.9	65°	16	0.1398

* Smith's Electro-Chemical Analysis, p. 61.

2 *Am. Chem. J.*, 12, 329.

Cadmium from Sulphuric Acid Solution.—Smith¹ describes the quantitative deposition of cadmium from its sulphuric acid solution. Cadmium oxide was dissolved in sulphuric acid. The solution contained two cc. of free sulphuric acid of sp. gr. 1.095.

The volume of the solution was twenty-five cc. In two hours the cadmium was completely precipitated. The amount of cadmium present was 0.0931 gram. The following conditions were found to give good results by this method. A solution of cadmium sulphate containing 0.1599 gram of metal after adding three cc. of sulphuric acid, sp. gr. 1.09, and diluting to 125 cc., was electrolyzed with a current of $N.D._{100} = 0.078$ A and $V = 2.61$. The temperature during the electrolysis was 65°. In five hours the deposition of cadmium was complete. The metal weighed 0.1604 gram.

BISMUTH.

Smith and Thomas² deposited bismuth from a citrate solution which contained an excess of sodium citrate. Bismuth hydroxide was dissolved in citric acid and sodium hydroxide added to alkaline reaction. Smith³ also states that bismuth may be precipitated from an alkaline citrate solution, and a solution containing free citric acid. The conditions under which the deposition took place are not recorded. The following experiments were accordingly made in order to obtain the proper working conditions.

Bismuth from an Ammonium Citrate Solution.—A bismuth nitrate solution was made, adding sufficient nitric acid to the salt to prevent the formation of a basic nitrate on the addition of water. To a solution of this salt containing 0.1882 gram of metallic bismuth were added three grams of citric acid and the solution made ammoniacal. It was diluted to 125 cc. The temperature was raised to 70° C. A current of $N.D._{100} = 0.02$ A and $V = 1.8$ was allowed to act for three hours. At the expiration of this time the current was increased to $N.D._{100} = 0.04$ A and $V = 2.3$. Finally, in order to deposit the last traces of the metal held in solution the current was made $N.D._{100} = 0.09$ A. The deposit of bismuth obtained in this way was light

¹ *Am. Chem. J.*, 2, 42.

² *Ibid.*, 5, 114.

³ Smith's *Electro-Chemical Analysis*, p. 69.

gray in color, very compact and adherent. In one case the current acted all night and the deposit was darker in color, but adherent and easily washed. There was a noticeable amount of the bismuth peroxide deposited. The anode was weighed therefore before and after the electrolysis, and from the weight of the bismuth peroxide found, the amount of the bismuth deposited in this way, calculated and added to the weight of that precipitated upon the cathode.

RESULTS.

Bismuth. Gram.	Citric acid. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Amount found. Gram.
0.1882	3	125	N.D. ₁₀₀ =0.02 (for 3 hours).	1.8	70°	16	0.1881
			N.D. ₁₀₀ =0.04 A.	2.3	all night in cold.		
			N.D. ₁₀₀ =0.06 A.				
0.1882	3	125	N.D. ₁₀₀ =0.02 A (for 3 hours).	1.6	70°	6½	0.1880
			N.D. ₁₀₀ =0.04 A.	2			
			N.D. ₁₀₀ =0.09 A.	3			
0.1822	3	125	N.D. ₁₀₀ =0.03 A.	2	65°	6	0.1819
			N.D. ₁₀₀ =0.042 A.	2.58			
			N.D. ₁₀₀ =0.09 A.	3			
0.1822	3	125	N.D. ₁₀₀ =0.03 A.	2	65°	6	0.1820
			N.D. ₁₀₀ =0.042 A.	2.6			
			N.D. ₁₀₀ =0.09 A.	3			

Bismuth from a Potassium Citrate Solution.—The solution of bismuth nitrate used contained 0.1777 gram. To this were added seven grams of citric acid, followed by an excess of potassium hydroxide. The solution was diluted to 125 cc. The temperature was 70°. The current for this solution was also low at the beginning and was gradually increased to 0.09 A. The deposit of bismuth peroxide on the anode was treated as indicated in the preceding method. The bismuth was in all cases a gray, compact, adherent deposit.

RESULTS.

Bismuth. Gram.	Citric acid. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.	Amount found. Gram.
0.1767	7	125	{ N.D. ₁₀₀ =0.02 A. N.D. ₁₀₀ =0.038 A.	2.16 2.18	65°	5	0.17648
0.1777	7	125	{ N.D. ₁₀₀ =0.02 A. N.D. ₁₀₀ =0.05 A.	2.5 3.	70°	5	0.1781
0.1777	7	125	{ N.D. ₁₀₀ =0.03 A. N.D. ₁₀₀ =0.05 A.	2.1 2.5	65°	5½	0.1774

Bismuth from a Citric Acid Solution.—Seven grams of citric acid were added to a solution of bismuth nitrate containing 0.1767 gram of bismuth. The solution at 70° was electrolyzed with a current N.D.₁₀₀ = 0.02 A and V = 1.8. Subsequently it was increased to N.D.₁₀₀ = 0.07 A and V = 2.6.

RESULTS.						
Bis- muth. Gram.	Citric acid. Grams.	Dilu- tion. cc.	Current.	Volt- age.	Tem- pera- ture.	Time. Hours.
0.1767	7	125	N.D. ₁₀₀ = 0.02 A.	1.8	65°	5
0.1767	5	125	N.D. ₁₀₀ = 0.38 A.	2.6		
			N.D. ₁₀₀ = 0.02 A.	1.8		
			N.D. ₁₀₀ = 0.05 A.	2.66	70°	5
						0.1761

Mercury from Nitric Acid Solution.—The fact that mercury could be determined satisfactorily from a nitric acid solution appears in the *Berichte*.¹ Mercuric nitrate was electrolyzed by Smith and Knerr.² There was one-half to one cc. of free nitric acid present. Bright, shining deposits of 0.0911 gram were obtained in thirty minutes. The current used for the purpose, liberated four cc. of oxyhydrogen gas per minute.

In the following work three cc. of concentrated nitric acid were added to a solution of mercuric chloride containing 0.1403 gram of metallic mercury. The solution (125 cc.) was electrolyzed with a current N.D.₁₀₀ = 0.06 A and V = 2 for four hours. The temperature was 70° C. The solution in the dish was siphoned off before the interruption of the current.

RESULTS.						
Mer- cury. Gram.	Nitric acid. cc.	Dilution. cc.	Current.	Volt- age.	Temper- ature.	Time. Hours.
0.1403	3	125	N.D. ₁₀₀ = 0.06 A.	2	70°	4½
0.1403	3	125	N.D. ₁₀₀ = 0.07 A.	1.91	70° ¹	4
						0.1406

Mercury from Sulphuric Acid Solution.—It has been known for a considerable time that mercury could be deposited from a solution feebly acidulated with sulphuric acid. The current which was used, generated five to six cc. of oxyhydrogen gas per minute. In repeating this method for the precipitation of mercury one cc. of sulphuric acid was added to a solution of mercuric chloride. A current of N.D.₁₀₀ = 0.4–0.6 A and V = 3.5 effected the deposition. The temperature during the operation

¹ *Ber. d. chem. Ges.*, 19, 329.

² *Am. Chem. J.*, 8, 206.

was 65° C. The mercury was entirely deposited in one hour. It had a brilliant metallic appearance. It was washed with cold water. The mercury present in the solution was 0.1403 gram. The deposit weighed 0.1402 gram.

Iron from a Citrate Solution.—In 1888 Smith reported the deposition of iron from a sodium citrate solution containing free citric acid. The solution used was ferric ammonium sulphate, and the current acting upon the solution gave six cc. of oxyhydrogen gas per minute.

The method was repeated, using a solution of the alum containing 0.0378 gram of metallic iron, ten cc. of sodium citrate, equivalent to 1.18 grams and three cc. of citric acid equivalent to 0.059 gram, and the solution diluted to 125 cc. With a current of $N.D._{100} = 0.58$ A and $V = 5.7$ in seven hours the deposition was complete. Another determination gave 0.0375 gram of iron, and a third gave 0.0379 gram. By titration with potassium permanganate the deposit was found to contain 0.03789 gram of iron. The carbon, therefore, in this deposit was 0.079 per cent.

Similar experiments were conducted, using 0.1035 gram of iron. The current used was $N.D._{100} = 0.8$ A and $V = 9$. The temperature was 60° during the electrolysis. The solution was 250 cc. The deposit weighed 0.1046 gram. By titration of the iron 1.06 per cent. of carbon was found. With identical conditions, using 0.1280 gram of iron 0.94 per cent. of carbon was found deposited in the metal.

RESULTS.

Iron. Gram.	Citrate. Grams.	Citric acid. Gram.	Current.	Tem- per- age.	Time. Hours.	Found. Gram.	Carbon. Per cent.
0.0378	10 cc.=1.18	3 cc.=0.059	$N.D._{100}=0.58$ A.	5.7	35°	7	0.0379 0.079
0.0378	10 cc.=1.18	3 cc.=0.059	$N.D._{100}=8-1.3$	9-11	70°	4	0.0383 1.1
0.1035	10 cc.=1.18	3 cc.=0.059	$N.D._{100}=8$	9-11	50°	4½	0.1046 1.06
0.1277	10 cc.=1.18	5 cc.	$N.D._{100}=0.4-1$ A.	7-11	50°	4½	0.1278 0.00
0.1277	10 cc.=1.18	5 cc.	$N.D._{100}=0.8$ A.	7-8	50°	4½	0.1280 0.94

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
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ACTION OF HYDROCHLORIC ACID GAS UPON SULPHATES, SELENATES, TELLURATES, AND PHOSPHATES.

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EXPERIMENTS have been made at various times in this laboratory upon the action of the gaseous haloid acids on metallic oxides and sulphides. Frequently new methods of separation have resulted. These have proved very satisfactory in every respect, from the standpoint of the analyst.

In the following paragraphs we give additional data collected from the same field, and trust that they may not be devoid of interest to the reader.

Knowing that selenic and telluric acids could be expelled from their salts by hydrochloric acid gas we endeavored to ascertain whether, if a sulphate were mixed with one or both of the preceding salts, it would be possible to drive out the selenic or telluric acid and leave the sulphate intact. Accordingly a perfectly dry mixture of a sulphate and a selenate was exposed to the action of well-dried hydrochloric acid gas. The selenic acid was not only expelled but also varying amounts of sulphuric acid were driven out. Thus, two trials were made with definite amounts of the salts. The results were these:

Potassium sulphate taken. Gram.	Potassium selenate taken. Gram.	Sulphur remaining in the salt acted upon. Per cent.
0.4323	0.4567	33.59
0.3338	0.1583	33.51

In brief, about sixty-five per cent. of the sulphur originally contained in the potassium sulphate was expelled in the presence of the selenate. When a tellurate was mixed with the sulphate and the two subjected to the action of hydrochloric acid gas, not only was the tellurium driven out from its combination but the sulphur also in amounts, which varied with the working conditions. The original idea, therefore, of effecting a separation was abandoned.

We next exposed pure, dry potassium sulphate to the influence

of the haloid acid. A weighed amount of the salt was introduced into a porcelain boat, placed in a combustion tube of hard glass, through which the gas was conducted in the cold. It was very soon observed that the salt had increased very considerably in weight (as much as twelve per cent). After a time the boat was removed and the residue in it analyzed. Thus, 1.0896 grams of potassium sulphate after exposure for three and one-half hours to the gas, in the cold, weighed 1.1162 grams—an increase of 0.0266 gram. The salt was dissolved in water and the hydrochloric acid in it determined. It equaled 0.0268 gram, or a difference of 0.0002 gram from the observed increase in weight. This product (an addition product evidently) maintained its composition when exposed to 130° in a drying oven. It did not lose in weight on standing over soda-lime, in a vacuum desiccator, for fifteen hours.

When dry potassium sulphate was heated in hydrochloric acid gas from 200° to a dull red heat, an examination of the water in the receiving vessel showed the presence of sulphuric acid, while the substance remaining in the boat after this treatment weighed more than the original substance. It gave an acid reaction to litmus and decolorized a red phenolphthalein solution. As much as nineteen per cent. of the sulphuric acid in the salt was expelled in this way. The quantity of acid driven out was greater in the presence of a selenate or tellurate, equaling in several instances seventy-five per cent.

This deportment of sulphuric acid confirms an early observation of Heusgen,¹ who found that "Kalium sulfat wird weder in der Kälte noch bei gewöhnlicher Temperatur von Salzsäure angegriffen bei 360° liess sich in dem vorgelegten Wasser schon eine wägbare Menge Schwefelsäure nachweisen, bei dunkler Rothgluth erfolgt jedoch die Zersetzung *fast* quantitativ in Chlormetall und freie Schwefelsäure." The gas evidently attacks the salt in the cold. This is proved by the formation of the addition product. We never observed a complete elimination of the sulphuric acid. It was not, indeed '*fast quantitative*.' And, Prescott,² trying the action of aqueous hydrochloric acid upon metallic salts, observed that upon evaporating a gram of sodium sulphate with 4.035 grams of

¹ *Ber. d. chem. Ges.*, (1876), 1671.

² *Chem. News*, 36, 178.

aqueous hydrochloric acid, containing 1.251 grams of hydrochloric acid, he obtained only 0.070 gram of sodium chloride, and 0.807 gram of undecomposed sulphate remained.

The question as to how the sulphuric acid is expelled from its salt is worth consideration. The thought first suggested was that the addition compound, $K_2SO_4 + HCl$, is produced when the gas acts upon the salt, and this upon the application of heat decomposes, forming potassium chloride and acid potassium sulphate, the latter being changed by the same heat into $2KHSO_4 = K_2SO_4 + H_2O + SO_2$. If this were true then the addition compound, which in theory was formed at first, when heated alone in dry air should give up its sulphuric acid in part at least and it should be found in the water of the receiver. Several trials were made. Sulphuric acid was not found in the receiver, but instead about eighty-six per cent. of the hydrochloric acid originally present with the potassium sulphate was discovered to be there. After numerous experiments of various sorts we concluded that this remarkable expulsion of sulphuric acid from one of its stable salts is to be attributed to mass action. This is emphasized by its more complete expulsion when a selenate or a tellurate is present.

It is a well-established fact that phosphoric acid is not expelled by the gaseous haloid acids from its salts.

A mixture of dry sodium tellurate and dry sodium pyrophosphate was exposed to the action of hydrochloric acid gas. Care was taken that the temperature did not become so intense as to melt the mass in the boat. When this occurs the telluric acid is apparently reduced very rapidly. In the analysis, which will be introduced, the tellurium was merely expelled. No attempt was made to estimate its amount. The residual phosphate, after solution in water, was invariably examined for tellurium but it was not detected. The phosphoric acid was determined in the usual manner.

ANALYSES.

	Phosphorus present in the $Na_2P_2O_7$. Gram.	Amount of sodium tellurate taken. Gram.	Phosphorus found as $Mg_2P_2O_7$. Gram.
1	0.1030	0.1247	0.1026
2	0.1197	0.1632	0.1199
3	0.1096	0.0832	0.1094

Sodium selenate was next mixed with sodium pyrophosphate. Much less time was required for the volatilization of the selenic acid than for that of the telluric acid. The temperature was gradually raised to 450°C. It was not allowed, nor was it necessary, to go beyond this point.

ANALYSES.

	Phosphorus present in the $\text{Na}_2\text{P}_2\text{O}_7$ used. Gram.	Sodium selenate. Gram.	Phosphorus found as $\text{Mg}_2\text{P}_2\text{O}_7$. Gram.
1	0.0728	0.1763	0.0729
2	0.1057	0.2017	0.1054
3	0.1198	0.1416	0.1199

The preceding results with phosphates and tellurates and those with selenates and phosphates leave no doubt as to the complete separation of their respective acids, in the manner indicated. The method is free from all disturbing factors and may be executed without difficulty.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 45.]

THE PRECIPITATION OF COPPER BY ZINC.

BY JOHN C. SHENGLE AND EDGAR F. SMITH.

Received August 2, 1899.

AT various times during the past year attempts have been made in this laboratory to make a direct comparison between silver and cadmium, with the hope that in this way the atomic mass of the latter metal might be definitely established. The most carefully purified metallic cadmium in weighed amounts was allowed to act upon various soluble salts of silver. The precipitation of the latter metal was rapid and complete. The results while very fair in a quantitative respect could not be used for the purpose designed. The precipitated silver contained cadmium. It was not undissolved portions of the latter but metal originating from the salt which was acted upon, which salt became in some way encased in the silver so that the most painstaking efforts failed to eliminate it. Nor did it seem to make any difference as to which silver salt was acted upon. Cadmium, in small amounts it is true, but nevertheless, cadmium was invariably discovered in the beautiful deposits of silver.

When copper salts were substituted for silver salts, the cadmium threw out the copper quickly and in calculated amounts, but it also was contaminated with varying quantities of cadmium, so that the scheme originally planned for the determination of the atomic mass of cadmium was abandoned.

This negative experience suggested the idea of testing the copper precipitated by metallic zinc. This being a method recommended for the quantitative estimation of copper we concluded to ascertain if possible whether it carried or retained any zinc. Pure copper sulphate was prepared, and metallic zinc was also obtained pure by the distillation method of Morse and Burton.¹

The determinations were conducted in the usual manner, but instead of weighing the precipitated copper it was dissolved in nitric acid and estimated by means of the electric current. The liquor poured off from this deposit was examined for the zinc.

ANALYSES.

I. Twenty cc. of a copper salt solution, containing 0.1739 gram of copper, was precipitated by metallic zinc. The deposit of copper was filtered, thoroughly washed, dried, and dissolved in acid, and its solution electrolyzed, the filtrate from the copper deposit being used for the determination of any contaminating zinc:

	Copper present. Gram.	Copper found. Gram.	Zinc found. Gram.
I.....	0.1739	0.1742	0.0067

In the second and third determinations the results were:

	Copper present. Gram.	Copper found. Gram.	Zinc found. Gram.
II.....	0.1739	0.1741	0.0027
III.....	0.2609	0.2612	0.0033

Twenty-two precipitations were made with varying conditions. Zinc was found in all of the precipitated copper. As a rule this method gives fair results, but it is notwithstanding interesting to know that the good results must be due largely to a balancing of errors.

¹ *Am. Chem. J.*, 10, 148, (1888).

THE PERSULPHATES OF RUBIDIUM, CESIUM, AND THALLIUM.

BY ARNOTT R. FOSTER AND EDGAR F. SMITH.

Received August 2, 1899.

SINCE Hugh Marshall prepared a number of persulphates these salts have attracted considerable attention both from a theoretical and practical standpoint. As the potassium and ammonium salts are generally those which are made and with which experiments are conducted we concluded to attempt the production of the persulphates of rubidium and cesium. We employed a "divided cell," using for the purpose that one recommended by Nernst which is so convenient that it should become a valuable adjunct in class experimentation.

RUBIDIUM PERSULPHATE.

To obtain this salt a solution consisting of two-thirds part sulphuric acid (1.35 sp. gr.) and one-third part of a saturated rubidium sulphate solution was electrolyzed, the cell being surrounded by a freezing-mixture of sodium chloride and ice.

Anode surface 1.575 sq. cm.....	0.45 A.
Voltage.....	8

A white precipitate began to separate at the anode after twenty minutes. The deposition at first was very slow, but later it became more rapid. The deposit was freed by filtration from the adherent liquid by washing it with cold water. Its aqueous solution oxidized a ferrous salt and liberated iodine from potassium iodide. The salt crystallized from water in acicular, vitreous forms.

Analysis.

The available oxygen was determined with ferrous ammonium sulphate and potassium permanganate. The oxidation proceeded slowly so that heat was applied to the solution of the persulphate and iron ammonium sulphate in an atmosphere of carbon dioxide. The oxygen liberated by ignition from a given quantity of the salt in an atmosphere of carbon dioxide was collected over caustic potash and measured.

I. 0.3381 gram of the persulphate on ignition gave 0.2484 gram of rubidium sulphate or 73.47 per cent., instead of 73.51 per cent., required by theory.

II. 0.2608 gram of the persulphate, acting upon ferrous ammonium sulphate (2.3633 grams), showed the presence of 0.0129774 gram of oxygen, equivalent to 4.69 per cent., instead of 4.41 per cent. (calculated).

III. A second titration of the persulphate was made with 0.2608 gram of the salt and 2.7190 grams of ferrous ammonium sulphate, when 0.11884 gram of oxygen was found, equivalent to 4.55 per cent., instead of 4.41 per cent.

IV. Oxygen by volume. 0.3254 gram of the persulphate gave 11.7 cc. of oxygen at 27° and 773 mm. pressure, or 0.01486784 gram equivalent to 4.56 per cent., instead of 4.41 per cent.

These results, therefore, conclusively demonstrate that rubidium persulphate, K,Rb_2O , or $KRbO_2$, really does exist.

V. Meyer's method was used in determining the solubility of this salt. 100 parts of water dissolved (1) 3.32 parts and (2) 3.49 parts of the salt at 22.5° C.

CESIUM PERSULPHATE.

It was formed by electrolyzing a chilled mixture of two-thirds part sulphuric acid (sp. gr. 1.35), and one-third part of a saturated cesium sulphate solution in the same manner as with rubidium sulphate.

Anode surface 1.57 sq. cm..... 0.32 ampere.

Voltage 6

A white deposit began to form at the anode in fifteen minutes. It separated even more rapidly than in the case of the rubidium persulphate. It was filtered out, washed thoroughly and analyzed. Its aqueous solution showed oxidizing properties, liberating iodine from potassium iodide and converting ferrous into ferric salts. The persulphate also crystallizes in colorless needles. Its analysis proved less satisfactory than that of the corresponding rubidium salt. It was difficult to obtain constant weight by ignition. The volume of oxygen was generally too high, although the results obtained by titration were entirely satisfactory.

Analysis.

I. 0.4348 gram of the salt and 2.0797 grams of ferrous ammonium sulphate, showed the presence of 0.0143 gram of oxygen, equivalent to 3.31 per cent., instead of 3.50 per cent.

II. 0.2612 gram of the persulphate and 2.1132 grams of ferrous ammonium sulphate showed 0.008439 gram of oxygen, equal to 3.59 per cent., instead of 3.50 per cent., by theory.

Upon determining the solubility of the persulphate by V. Meyer's method, it was found that 100 parts of water dissolved 8.71 parts of the salt at 23° C.; again, 100 parts dissolved 8.98 parts of the persulphate at the same temperature.

THALLIUM PERSULPHATE.

As thallium in some respects resembles the alkali metals, it occurred to us that perhaps it might also yield a persulphate. Accordingly, a saturated solution of its sulphate, treated with sulphuric acid (sp. gr. 1.70), as in the preceding examples, was chilled and electrolyzed.

Anode surface 1.57 sq. cm.....	0.45 A.
Voltage.....	14

At the expiration of an hour a white precipitate began to separate at the anode. It proved to be very soluble in water, and difficulty was experienced in getting it pure. In fact it decomposed so rapidly in the air that the analysis of it was abandoned. Its aqueous solution rapidly oxidized ferrous salts and set iodine free from potassium iodide. More than this we cannot offer for this salt which is undoubtedly produced in the oxidation of thallous sulphate.

THE CHROMIC ACID TEST FOR COCAINE.

BY GEORGE L. SCHAEFER.

Received July 7, 1899.

SINCE the publication of my proposed new test for cocaine, several articles have appeared in criticism thereof, which call for some reply.

P. W. Squire¹ states that the test "produces a turbidity in solutions of the best commercial samples of cocaine hydrochlorate." Further than this he does not go, but in a note appended

¹ "The New Test for Cocaine," *Chemist and Druggist*, April 22.

to his communication, the editor states that the "value of the chromate test is questionable." A. J. Crownley,¹ objects on the ground that the test is too delicate and that only a "synthetic" cocaine would stand it. The most satisfactory reply to these critics is the statement that the finest commercial brands of cocaine hydrochloride satisfactorily answer the chromic acid test.

E. Merck,² in criticizing the test states that the strength of the hydrochloric acid will affect the results obtained. In applying the test he found that a solution of cocaine to which he had added five cc. of ten per cent. hydrochloric acid, yielded negative results, and that upon increasing the amount of acid by using five cc. twelve and one-half per cent. hydrochloric acid, a turbidity was produced, thus in the first case showing the cocaine to be pure, and in the second case indicating impurities. This is in accord with my own observations, and the difference in the results is due to the fact that the sample of cocaine employed contained only very minute traces of amorphous alkaloids, the chromates of these latter bodies being far less soluble in the solution containing the higher percentage of hydrochloric acid. The turbidity will therefore be produced more rapidly and more distinctly than in the solution containing the weaker acid. An acid of ten per cent. strength was decided upon, as it is sufficient to indicate such very small traces of amorphous impurities, that only the very best brands of cocaine in the market will stand this test, and it, together with the permanganate test, guarantees a purity of product which cannot be obtained when McLagan's test is taken as the standard. If the reaction is carried out with a stronger acid, it is necessary to do so side by side with a specimen of chemically pure cocaine as at a low temperature cocaine chromate causes a turbidity in the more acid solution.

Merck further claims that the results are influenced by the age of the chromic acid solution. My own experience has failed to prove that such is the case. In a recent series of experiments with a number of samples of cocaine, using the same solution of chromic acid for fourteen consecutive days, and always applying the test side by side with a freshly prepared chromic acid solu-

¹ "Note on a New Test for Cocaine," *Pharmaceutical Journal*, April 15.

² "Cocaine Tests," *Pharm. Zig.*, No. 42.

tion, at no time was there noticed any difference in the results obtained.

In applying the test it is important that the temperature of the cocaine solution be maintained at 15° C., the chromates of both pure cocaine and the amorphous alkaloids being influenced by rise and fall of temperature, heat increasing and cold diminishing their solubility. The test produces no turbidity when the acid is added to a solution of a pure specimen of cocaine, the temperature being 15° C. If, however, the solution be subjected to a considerably lower temperature, it becomes turbid, and if it be preserved at this reduced temperature for several hours, a crystalline deposit will be found, consisting of long needle-shaped crystals of cocaine chromate. A solution of impure cocaine rendered turbid by the reagent at 15° C., and exposed to a lower temperature remains turbid for several hours, then slowly deposits a yellowish-brown amorphous sediment. These reactions are characteristic and serve to distinguish between cocaine and the amorphous alkaloids, especially isatropylcocaine. If a stronger acid is used the alkaloids will separate out quicker.

In order to show the superiority of the chromate test over McLagan's test, I prepared a series of specimens of cocaine of different degrees of purity. These, as well as the various brands of cocaine in the market, I subjected to McLagan's and the chromate test. As a result, I found specimens which gave negative results with McLagan's test, to be impure by the chromate test, and those specimens which reacted with McLagan's test yielded a decided turbidity upon the addition of even less than five cc. of the ten per cent. hydrochloric acid.

NOTES.

On the Reichert Figure of Butter.—During the last few years I have had occasion to examine a great many samples of butter, intended for exportation to Venezuela and other South American ports. As many of these samples were of very low grade, it occurred to me that a compilation of the Reichert figures obtained might be of interest to those engaged in this line of work, and I therefore take pleasure in submitting to the society the results of some 317 analyses, taken at random from my

laboratory books, and representing butter exported by five firms during the years 1897, 1898, and 1899.

The figures obtained are as follows :

15.2	14.7	13.1	15.3	16.6	12.5	15.6	12.5
15.2	13.9	13.6	14.7	15.8	13.6	16.0	12.2
13.8	14.0	13.4	14.9	17.0	15.1	15.0	12.3
14.8	13.3	17.0	14.3	16.1	16.6	16.2	13.4
13.0	13.9	17.8	13.6	17.0	15.2	16.6	13.6
13.8	14.3	13.7	13.7	17.0	14.6	14.8	13.7
13.8	14.2	13.2	15.3	15.3	13.5	17.0	16.2
13.7	14.3	13.2	16.3	16.1	16.2	14.6	17.5
14.4	13.9	15.8	15.9	13.6	13.9	14.2	15.9
14.0	14.9	14.7	15.1	15.4	13.9	13.8	14.6
16.6	13.1	12.6	16.4	13.6	14.7	15.3	13.9
14.3	15.6	16.2	14.7	15.6	15.8	16.4	15.7
15.4	14.0	16.2	15.2	14.2	13.6	15.8	14.7
14.0	14.2	14.2	12.0	14.3	16.7	14.0	18.2
14.2	12.6	12.0	13.8	14.7	16.9	14.0	15.5
15.4	15.0	15.1	13.2	15.0	14.5	15.0	14.0
16.5	15.2	14.5	13.2	13.9	16.0	15.1	13.0
13.2	15.3	12.5	16.0	14.8	16.2	15.0	14.0
12.6	15.6	12.8	13.6	13.5	15.0	15.9	17.2
14.4	13.8	11.2	17.2	12.4	13.8	13.0	11.7
14.2	14.0	12.8	15.3	14.0	14.2	12.8	15.0
13.6	14.0	13.5	15.7	14.1	17.6	14.7	15.4
14.7	16.2	12.7	15.5	14.0	15.8	15.6	13.8
14.8	15.9	13.0	16.6	16.0	13.7	14.8	16.0
14.7	17.0	13.1	15.5	13.8	13.9	15.0	14.3
13.4	15.5	14.6	15.5	13.6	14.9	14.8	14.9
14.8	14.2	15.5	13.4	15.0	15.5	15.0	13.5
15.2	13.8	16.6	13.8	15.4	13.4	16.2	13.8
16.6	15.2	16.0	14.2	13.6	14.8	16.6	13.5
14.9	13.4	16.2	15.8	12.5	14.5	16.0	16.3
14.8	11.4	16.0	13.0	14.3	12.8	17.4	16.5
13.8	13.4	15.7	15.0	15.1	14.2	17.7	16.2
16.9	13.8	14.7	14.0	14.3	15.6	15.8	15.7
14.6	13.6	14.0	13.6	16.4	14.0	16.9	13.6
16.2	13.5	13.5	12.8	13.4	13.3	15.4	12.8
16.1	13.8	14.1	14.9	15.8	14.7	14.7	14.5
15.4	14.0	14.5	14.1	15.4	15.6	15.7	16.1
16.6	14.5	15.0	15.6	14.1	15.6	13.6	
16.2	15.1	15.5	13.0	13.0	14.1	15.0	
15.6	14.7	15.3	14.6	12.8	16.4	12.0	

The average of these 317 tests is 14.7. The highest figure obtained was 18.2, and the lowest figures found were 11.2, 11.4, and 11.7.

The butters which gave these last three figures I at first blush suspected of being adulterated with some foreign fat, but subsequent tests showed this not to be the case. The three butters in question were all samples of winter butter, the one giving the figure 11.2 having been kept so long that it was on the verge of becoming tallowy, while the other two were decidedly rancid.

Although the above were samples of unadulterated butter, I, nevertheless, refused to pass them on the strength of the Reichert figure alone, as they were so far below the standard usually accepted by chemists.

Reichert found true butters to give numbers ranging from 13.55 to 14.55, with an average of 14, and declared any butter giving less than 12 must be adulterated.

Dr. G. C. Caldwell reported to the N. Y. State Board of Health estimations of twenty-seven samples of butter, yielding Reichert figures running from 12.7 to 15.5.

Waller and Martin (Report N. Y. State Dairy Commission, 1886) obtained from twenty-six samples of American butters Reichert figures of 12.2 to 16.3.

Prof. C. B. Cochran, West Chester, Pa., Food Inspector of the Pa. Board of Agriculture, has found the extreme minimum of the Reichert numbers of known genuine butters to be 12.5, and this chemist holds that the proper minimum is 11.5.

From the above it will be seen that there is a divergence of views as to what properly constitutes the lowest allowable Reichert figure for butters of known genuineness, but, from my own experience, I am in favor of placing the limit at 11.5.

I do not consider that it would be prudent to go much below this, so as to cover such extreme cases as I have just mentioned, as in cases of this kind it would not do to rely upon the Reichert number alone, the chemist only consenting to pass upon such products after satisfying himself as to their purity, by submitting them to a thorough examination. JAMES H. STEBBINS, JR.

Analysis of Zinc for Cadmium and Lead.—Place fifty grams zinc in a large beaker with 700–800 cc. water and 120 cc. hydrochloric acid (1.20 sp. gr.) and allow to stand over night. The greater portion of zinc is dissolved and removed by decantation. The lead and cadmium are precipitated on residual zinc.

After solution of the lead, cadmium, and residual zinc in dilute

nitric acid, sulphuric acid is added and nitric acid evaporated off. The lead and cadmium sulphates are boiled with water to dissolve cadmium sulphate, and after cooling, lead sulphate is filtered off and determined in the usual manner.

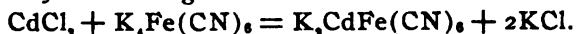
The cadmium in the filtrate is precipitated by hydrogen sulphide and after precipitation, the filter containing the precipitate is placed in a flask and cadmium sulphide dissolved in hydrochloric acid. After driving off the hydrogen sulphide by boiling, fifty cc. of a solution of zinc chloride containing ten grams zinc per liter is added, and cadmium and zinc titrated together with potassium ferrocyanide solution containing 36.76 grams potassium ferrocyanide per liter.

The ferrocyanide solution is standardized by titrating 50 cc. of the zinc solution, the difference between the amount required for the zinc solution and the solution containing cadmium and zinc is the amount required for cadmium precipitation. Each cc. of the ferrocyanide solution should precipitate 0.01 gram cadmium or 0.0085 gram zinc, zinc requiring 4.328 grams potassium ferrocyanide to precipitate one gram zinc.

The titration of small quantities of cadmium without addition of either zinc or more cadmium is inaccurate.

TITRATION OF CADMIUM BY POTASSIUM FERROCYANIDE.

The formula of cadmium ferrocyanide as usually given is $K_2CdFe(CN)_6$, the reaction between cadmium salts and potassium ferrocyanide being thus:



This will require 3.767 gram-molecules of potassium ferrocyanide to precipitate one gram-molecule of cadmium. In practice by titration of a commercially pure cadmium it was found to take 3.676 gram-molecules or a difference of two and one-half per cent.

The titration is as follows: 3.676 grams of potassium ferrocyanide are dissolved in a liter of water and the hot cadmium solution is titrated after addition of ammonium chloride in the same manner as zinc, using uranium acetate as indicator, the end-reaction being distinct. The cadmium ferrocyanide is white, as is zinc ferrocyanide, and as a result, zinc analyses by the ferrocyanide method will be high in proportion as cadmium is present.

P. A. MACKAY.

BOOKS RECEIVED.

Improvement in the Chemical Composition of the Corn Kernel. Bulletin No. 55, University of Illinois Agricultural Experiment Station, Urbana, Ill. June, 1899. 36 pp.

Recent Work on the San Jose Scale in Illinois. Bulletin No. 56, University of Illinois Agricultural Experiment Station, Urbana, Ill. July, 1899. 47 pp. 4 plates.

Descriptive General Chemistry. A Text-book for Short Course. By S. E. Tillman, Professor of Chemistry, Mineralogy, and Geology, United States Military Academy. Second edition. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1899. x+429 pp. Price \$3.00.

The Mineral Industry, its Statistics, Technology, and Trade, in the United States and Other Countries to the end of 1898. Edited by Richard P. Rothwell, editor of Engineering and Mining Journal; etc. Vol. VII, supplementing Vols. I to VI. New York and London: The Scientific Publishing Co. 1899. xxviii+909 pp. Price \$5.00.

Inorganic Chemical Preparations. By Felix Lengfeld, assistant professor of inorganic chemistry in the University of Chicago. New York: The Macmillan Company. 1899. xviii+57 pp. Price 60 cents.

Whole Corn Compared with Corn Meal for Fattening Hogs. By J. H. Stewart and Horace Atwood. Bulletin No. 59, June 1899, West Virginia Agricultural Experiment Station, Morgantown, W. Va. 11 pp.

Poultry Experiments. By J. H. Stewart and Horace Atwood. Bulletin No. 60, June, 1899, West Virginia Agricultural Experiment Station, Morgantown, W. Va. 20 pp.

The Sugar Beet in Montana. Bulletin No. 19, Montana Agricultural Experiment Station of the Montana College of Agriculture. Bozeman, Mont. October, 1898. 40 pp.

The Rise and Development of the Liquefaction of Gases. By Willett L. Hardin, Ph.D. New York and London: The Macmillan Co. 1899. x+250 pp. Price \$1.50.

The Elements of Qualitative Analysis. By William A. Noyes, Ph.D., professor of chemistry in the Rose Polytechnic Institute. Fourth edition, revised. New York: Henry Holt & Co. 1898. 87 pp. Price 88 cents.

A Treatise on the Kinetic Theory of Gases. By S. H. Burbury, M.A., F.R.S., late fellow of St. John's College, Cambridge. Cambridge: At the University Press. viii+157 pp. Price eight shillings.

ERRATUM.

In the June number, 1899, page 519, line 18 from bottom, for "fifty grains" read "fifty grams."

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 47.]

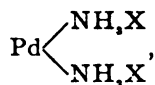
DERIVATIVES AND ATOMIC MASS OF PALLADIUM.

BY WILLETT LEPPLEY HARDIN.

Received July 14, 1899.

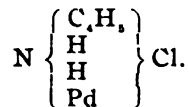
I. DERIVATIVES OF PALLADIUM.

THE ammonium derivatives of palladium have been very thoroughly investigated, and various classes of compounds have been prepared. The pallad-diammonium compounds are probably the most important of these derivatives. The constitution of this class of compounds is usually represented by the formula



where X is a univalent radical (usually chlorine, bromine, or iodine).

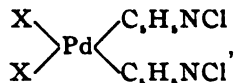
The palladium derivatives of organic bases have been investigated only to a very limited extent. In 1853 Müller¹ prepared a compound of ethylamine and palladous chloride, and suggested the formula



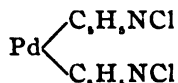
¹ *Ann. Chem.* (Liebig), 86, 366 (1853).

He also prepared the aniline derivative of palladous chloride, and described it as a yellow crystalline compound. No analyses were made of these compounds, but Müller considered them as analogous to the pallad-diammonium derivatives.

Quite recently Rosenheim and Maass,¹ have prepared a number of derivatives of pyridine with quadrivalent palladium. These compounds are represented by the formula



where X represents chlorine, bromine, or iodine. These experimenters also prepared and analyzed the compound

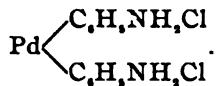


This appears to be the only derivative of bivalent palladium with an organic base, which has been analyzed. The compound was prepared by treating palladous chloride, dissolved in aqueous hydrochloric acid, with pyridine. It consists of a bright yellow crystalline powder.

In the present investigation several derivatives of bivalent palladium with organic bases have been prepared and analyzed. The compounds correspond to the pallad-diammonium salts, and are named as derivatives of these compounds.

Diphenyl-pallad-diammonium Chloride.

When a slight excess of aniline is added to a hydrochloric acid solution of palladous chloride, a voluminous yellow precipitate is formed. The compound is insoluble in hydrochloric acid, but soluble in ammonium hydroxide. When heated in a platinum spoon the substance takes fire and burns with a smoky flame. The compound is similar in appearance to the pallad-diammonium derivative, and its analysis gave results corresponding to this class of compounds. The constitution therefore may be represented by the formula



The results of the analysis are as follows :

¹ *Ztschr. anorg. Chem.*, 18, 331 (1898).

	Calculated.	Found.
Palladium.....	29.39	29.5
Chlorine	19.47	19.32

It may be mentioned also that aniline precipitates palladium quantitatively.

Diphenyl-pallad-diammonium Bromide.

This compound was prepared in a manner similar to that of the chloride; that is, by precipitating the hydrobromic acid solution of palladous bromide with aniline. The substance is similar to the chloride in appearance. The results of the analysis, and those calculated from the formula $\text{Pd}(\text{C}_6\text{H}_5\text{NH}_2)_2\text{Br}_2$, are as follows:

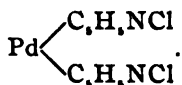
	Calculated.	Found.
Palladium.....	23.62	23.8
Bromine	35.27	35.4

Dipyridine-pallad-diammonium Chloride.

The preparation and analysis of this compound correspond exactly with the work of Rosenheim and Maass. The substance is pale yellow in color, and soluble in excess of pyridine or in ammonium hydroxide. The analysis gave:

	Per cent.
Palladium	32.0
Chlorine.....	20.8

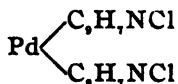
This corresponds to the formula



The theoretical values for palladium and chlorine from this formula are 32 and 21.1 per cent. respectively.

Diquinoline-pallad-diammonium Chloride.

When quinoline is added to a hydrochloric acid solution of palladous chloride a pale yellow precipitate is formed, which dissolves in excess of the quinoline to a colorless solution. On adding hydrochloric acid to the solution the substance is reprecipitated. The values obtained for the percentage of palladium and chlorine, and those calculated from the formula

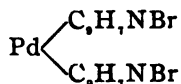


are as follows:

	Calculated.	Found.
Palladium.....	24.5	24.8
Chlorine	16.26	16.0

Diquinoline-pallad-diammonium Bromide.

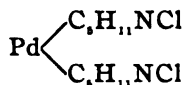
This compound was prepared from the palladous bromide and hydrobromic acid, in a manner similar to that outlined in the preparation of the chloride. Its physical properties are similar to those of the chloride. The analysis gave 20 per cent. palladium and 30.4 per cent. bromine. The theoretical values for the formula



are 20.38 and 30.05 per cent. respectively.

Dipiperidine-pallad-diammonium Chloride.

On adding piperidine to a hydrochloric acid solution of palladous chloride a pale yellow precipitate is formed, which is soluble in excess of piperidine. The substance is reprecipitated by hydrochloric acid. The palladium content was found to be 31 per cent. while that calculated from the formula

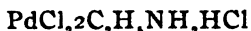


is 30.73 per cent.

The compounds which have been described are all derivatives of pallad-diammonium compounds. Hydrogen does not attack these substances at the ordinary temperature, but when brought in contact with them in a combustion tube a very small flame is sufficient to induce the reaction. The analyses were made by reducing the compounds to metal in a current of hydrogen. The volatile products were conducted into solutions of silver nitrate where the halogen content was precipitated. In order to prevent the occlusion of hydrogen the resulting metal, in every case, was allowed to cool in a current of air.

No experiments were made with the free amines of the fatty series, but one compound was prepared by a solution of palladous chloride with ethylamine hydrochloride. When the solution was partially evaporated, brownish red scales separated. These

were dissolved in water and recrystallized. The resulting crystals were analyzed and found to contain 30.3 per cent. palladium and 40.94 per cent. chlorine. The corresponding values calculated from the formula



are 31.4 and 41.58 per cent. The substance is evidently a double salt corresponding to the double chloride of ammonium and palladium.

The foregoing observations, while limited to five organic bases, indicate that bivalent palladium reacts with organic amines and other bases, in a manner similar to that with ammonia.¹ The diphenyl-pallad-diammonium chloride and the corresponding bromide can be prepared with little difficulty. Both are anhydrous and insoluble in water, and can be dried at 100° without decomposition. The compounds seem to be well adapted to atomic mass determinations.

II. THE ATOMIC MASS OF PALLADIUM.

Inasmuch as the earlier determinations of the atomic mass of palladium show considerable variation, it was thought advisable to make use of some of the compounds described in part I of this paper in a redetermination of this constant. After some preliminary observations the diphenyl-pallad-diammonium chloride and the corresponding bromide were selected as being most suitable for quantitative determinations.

Historical Statement.

In 1828 Berzelius² made the first reliable determinations of the atomic mass of palladium. The method consisted in analyzing the double chloride of palladium and potassium. The results show considerable variation. The ratio between the palladium and the potassium chloride gave 106.22 as a mean for the atomic mass of palladium.³

Sixty years later Keiser⁴ investigated the compound employed by Berzelius, and found that it contained "water of decrepita-

¹ Palladous chloride solutions were also precipitated with phenylhydrazine, but the compound was not analyzed.

² *Pogg. Ann.*, 13, 454.

³ The atomic mass of oxygen is taken as sixteen in all the calculations in this paper.

⁴ *Am. Chem. J.*, 11, 398 (1889).

tion." Keiser concluded that the potassium palladium chloride is not suitable for atomic mass determinations, and made use of pallad-diammonium chloride. The salt was carefully dried at a temperature of from 120° to 130° . The analyses were made by reducing known quantities of the substance in a current of hydrogen, and weighing the resulting metal. The mean of two series of observations gave 106.54 for the atomic mass of palladium.¹

In 1892 Keller and Smith,² investigated the various methods of purifying palladium, and concluded that the method employed by Keiser does not give a product which is free from foreign metals, especially copper. These experimenters made use of an entirely different method of purification, and probably obtained purer material than any that had been employed in the earlier determinations. After obtaining the pure metal it was converted into pallad-diammonium chloride. The material was carefully dried, and the palladium content determined by the electrolysis of the ammoniacal solution in a silver-coated platinum dish. The mean of nine determinations gave 107.18 for the atomic mass of palladium. Two experiments were made by converting pallad-diammonium chloride into palladium sulphide, by means of hydrogen sulphide. The results were about two-tenths of a unit higher than those obtained by electrolysis. The weighings were not reduced to a vacuum standard.

During this same year Bailey and Lamb³ made two series of observations on the atomic mass of palladium. They experimented with pallad-diammonium chloride, and determined both the chlorine and palladium. The chlorine determinations gave 106.65, while the palladium determinations gave only 105.75 for the atomic mass of palladium. The weighings were reduced to a vacuum standard.

In 1893, Joly and Leidie⁴ repeated the earlier determinations on the double chloride of potassium and palladium. The perfectly dry salt was dissolved in water acidulated with hydrochloric acid, and the solution electrolyzed. From the weight of

¹ This value is based upon Clarke's reductions to a vacuum standard.

² *Am. Chem. J.*, 14, 423 (1892).

³ *J. Chem. Soc.*, 61, 745 (1892).

⁴ *Compt. rend.*, 116, 147 (1893).

the metal obtained the authors gave 106.28 for the atomic mass of palladium.

During the next year Keiser and Breed¹ repeated the earlier work on the reduction of pallad-diammonium chloride. The material was carefully purified by two different methods. The mean of two series of experiments is almost identical with the value obtained by Keiser in his earlier experiments.

A glance at the foregoing results will show considerable variation. The values usually accepted for the atomic mass of palladium are as follows :

Clarke.....	106.36
Richards	106.5
German committee	106.0

No satisfactory explanation has yet been offered to account for these variations. Keller and Smith suggested that there may be a slight loss of material in the reduction of pallad-diammonium chloride. Keiser, however, in his second series of determinations, failed to detect any indications of such a loss. It has also been suggested that the high value obtained by Keller and Smith may have been due to the occlusion of hydrogen by the metallic palladium. Careful precautions, however, were taken to prevent any error from this source, and the authors were unable to detect the presence of hydrogen in the metallic deposit. The reliable determinations of the atomic mass of palladium are based almost entirely upon analyses of pallad-diammonium chloride. The variations then must be due either to the method of analysis or to the method of purifying the material. In the present investigation the metal was purified by the method of Keller and Smith, and the analyses were made in a manner similar to those of Keiser. The value obtained is higher than that usually accepted for the atomic mass of palladium. This would indicate that the results are influenced by the method of purifying the material.

Purification of Metallic Palladium.

As already mentioned the material used in these experiments was purified by the method outlined by Keller and Smith. The commercial metal, about twenty-five grams, was dissolved in

¹ *Am. Chem. J.*, 16, 20 (1894).

aqua regia, and the solution evaporated to dryness on a water-bath. The residue, after evaporating several times with hydrochloric acid, was dissolved in water containing a little hydrochloric acid. The solution was diluted with water, and treated with an excess of ammonium hydroxide. Heat was applied until the palladium salt was completely dissolved. A small quantity of reddish brown material remained insoluble. This was filtered out and the filtrate treated with an excess of hydrochloric acid, when the yellow pallad-diammonium chloride was precipitated. After standing for forty-eight hours the compound was filtered out and thoroughly washed. It was then dissolved in cold, dilute ammonia water, the solution filtered, and the palladium reprecipitated as pallad-diammonium chloride.

This salt was dried and carefully ignited in the air, after which the bluish green residue was reduced in a current of hydrogen. The resulting metal was dissolved in aqua regia and the solution evaporated to dryness on a water-bath. The residue was digested with hydrochloric acid and evaporated to dryness several times. The remaining chloride was then dissolved in water containing a little hydrochloric acid, and the solution carefully neutralized with sodium carbonate. The calculated amount of mercuric cyanide was then added, and the palladium was precipitated as palladous cyanide. After standing for several days the precipitate was repeatedly washed by decantation and finally on a filter. The palladous cyanide was dried and strongly ignited for several hours in a muffle-furnace.

The metal which resulted from the ignition of the palladous cyanide was extracted with hydrochloric acid, to remove any copper oxide that might have been present, and then dissolved in aqua regia. After repeated evaporations with hydrochloric acid, a dilute solution of the palladous chloride was saturated with sulphur dioxide. The solution became yellow in color and a slight precipitate was formed on standing. Potassium thiocyanate produced a slight turbidity when added to the yellow solution. No attempt was made to determine the composition of these precipitates.¹ Upon warming, the solution lost its color.

When the sulphur dioxide had been completely removed by

¹ In the experiments of Keller and Smith these precipitates were examined and found to contain both gold and copper.

boiling, the solution was filtered, and the palladium precipitated from the neutralized filtrate by means of potassium formate. The metal came down in black flakes. The palladium thus obtained was thoroughly washed, dried, and strongly ignited for several hours in a closed porcelain crucible in a muffle-furnace. The resulting metal after treating with hydrochloric acid was heated in a current of hydrogen, when it became almost silver-white in color.

Preparation of Diphenyl-pallad-diammonium Chloride.

Pure metallic palladium, obtained in the manner just outlined, was dissolved in hydrochloric acid containing a small quantity of nitric acid. These acids had been previously purified. The resulting solution was evaporated to dryness on a water-bath. The residue was digested with hydrochloric acid and again evaporated to dryness. This was repeated until the nitric acid was completely expelled. The resulting palladous chloride was dissolved in water acidulated with hydrochloric acid. The solution after filtering was treated with a slight excess of aniline which had been purified by several redistillations.

The resulting diphenyl-pallad-diammonium chloride was allowed to stand for twelve hours in a covered beaker. It was then washed several times by decantation, and afterward washed upon a filter. The final washings were made with alcohol. The resulting material was dried for several days at the ordinary temperature, and finally dried for forty-eight hours in an air-bath at a temperature of 90°.

Method of Analysis.

The analyses were made by reducing known quantities of the substance in a current of hydrogen, and weighing the resulting metal. The material was placed in a porcelain boat which, in turn, was placed in a hard glass combustion tube. A current of pure, dry hydrogen gas was then conducted through the tube. There was no action at the ordinary temperature, but a very small flame under the tube was sufficient to induce the reaction. The temperature was gradually increased. After the reduction appeared to be complete the temperature was kept at a bright red heat for one hour. The flames were then removed, and

when the temperature had fallen below a red heat the current of hydrogen was replaced by a current of dry air. The metal was then heated to a bright red heat for a period of two hours. This precaution was taken in order to remove any carbon which might have resulted from the decomposition. It might be remarked, however, that there were no indications of free carbon in the boat. After heating in the air the metal was again heated in a current of hydrogen, and finally cooled in a current of air to prevent any occlusion of hydrogen. The resulting metal was almost silver-white in color.

In the first experiments an attempt was made to determine the quantity of chlorine by conducting the volatile products into solutions of silver nitrate. The results, however, were not accurate enough for atomic mass determinations. The values which follow are all based upon determinations of metallic palladium. The weighings were made on a short-armed Troemner balance with a set of calibrated weights. The balance is sensitive to the fortieth of a milligram. All weighings have been reduced to a vacuum standard. In order to make these reductions the density of diphenyl-pallad-diammonium chloride was determined and found to be 1.66.

First Series.

The atomic masses used in the calculation of results are those given in Clarke's report for 1898.¹ The results from seven analyses of diphenyl-pallad-diammonium chloride are as follows :

	Weight of substance. Grams.	Weight of palladium. Gram.	Atomic mass of palladium.
1	0.98480	0.28953	107.06
2	1.10000	0.32310	106.92
3	1.02820	0.30210	106.96
4	1.19230	0.35040	107.00
5	1.40550	0.41300	106.98
6	1.26000	0.37040	107.04
7	2.25510	0.66310	107.08
Mean		107.006	
Maximum			107.08
Minimum			106.92
Difference			0.16

¹ This Journal, 21, 200.

Preparation of Diphenyl-pallad-diammonium Bromide.

This compound was prepared in a manner analogous to that of the chloride. The hydrobromic acid was prepared by the action of pure bromine on anthracene. The acid fumes were conducted through tubes of anthracene to remove the free bromine. It is necessary in these experiments to use hydrobromic acid which is absolutely free from bromine, for, according to Rosenheim and Maass, these compounds take up free bromine to form addition products. This precaution was carefully observed.¹ The washing and drying of the material were carried out just as in the case of the chloride. The specific gravity of the compound was found to be 1.75.

Second Series.

Five analyses of diphenyl-pallad-diammonium bromide gave the following values for the atomic mass of palladium :

	Weight of substance. Grams.	Weight of palladium. Gram.	Atomic mass of palladium.
1	0.88567	0.20917	107.01
2	1.31280	0.31000	106.99
3	1.50465	0.35540	107.03
4	2.01635	0.47635	107.05
5	2.92300	0.69080	107.10
Mean		107.036	
Maximum			107.10
Minimum			106.99
Difference			0.11

Ammonium Palladium Bromide.

This salt was prepared in a pure condition by Smith and Wallace¹ as follows: Pure metallic palladium was dissolved in nitro-hydrobromic acid. The resulting solution was evaporated, and the residue repeatedly moistened with hydrobromic acid and evaporated to dryness on a water-bath. The resulting palladium bromide was dissolved in water containing a little hydrobromic acid, and to the solution was added an equivalent quantity of ammonium bromide. On evaporating the solution large olive-

¹ Before the publication of Rosenheim and Maass had been noticed, a series of experiments were made with hydrobromic acid which contained a small quantity of free bromine. The results obtained for the atomic mass of palladium were somewhat variable, and about one unit lower than those obtained from the chloride.

² This Journal, 16, 465 (1894).

brown crystals of ammonium palladium bromide separated. The salt was dissolved in water and recrystallized. The resulting material was carefully dried, and found to be anhydrous and stable in the air. The specific gravity of the salt is 3.40.

Third Series.

This series was made with the above salt two years ago. The results of four experiments reduced to a vacuum standard are as follows :

	Weight of substance. Grams.	Weight of palladium. Gram.	Atomic mass of palladium.
1	0.77886	0.18006	107.03
2	1.53109	0.35381	106.96
3	2.75168	0.63614	107.03
4	1.88136	0.43478	106.98
Mean		107.00	
Maximum.....			107.03
Minimum			106.96
Difference.....			0.07

SUMMARY.

By combining the three series we obtain, as a mean of all the results, the following value :

First series.....	107.006
Second "	107.036
Third "	107.000
Mean.....	107.014

This value is higher than that usually accepted for the atomic mass of palladium. The earlier determinations are based almost entirely upon analyses of pallad-diammonium chloride, while in the present investigation new factors have been introduced. Both carbon and bromine are important elements of comparison in these determinations. Further investigation will probably be necessary to fully explain the variation in the results of the different experimenters. The fact, however, that the three series of results in the present work agree very closely with each other, and approximately with the value obtained by Keller and Smith, and the fact that there is no apparent source of error in the method employed, furnish a strong argument in favor of the

value 107 for the atomic mass of palladium. This value does not influence the position of palladium in the periodic system.

In conclusion I desire to express my obligations to Professor Edgar F. Smith for suggesting this line of work, and for many valuable suggestions during its prosecution.

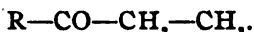
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

THE ACTION OF SODIUM METHYLATE UPON DIBROMIDES OF PROPENYL-COMPOUNDS AND OF UNSATURATED KETONES.

BY F. J. POND, O. P. MAXWELL, AND G. M. NORMAN.

Received July 28, 1899.

It was stated in a previous paper¹ that certain phenol ethers, which contain a C_6H_5 group having the propenyl structure, give bromine addition products which, on treatment with sodium alcoholate, yield ketones of the general formula,



Thus, the dibromides of anethol,² methyl-,³ ethyl-,³ and benzyl-¹ isoeugenol and isosafrol¹ form ketones when they are treated with sodium alcoholate. As the bromine derivatives of the corresponding isomeric compounds containing the allyl group are not converted into ketones by a similar treatment, this reaction is characteristic for those compounds containing the propenyl group. Therefore, the structure of the unsaturated group, C_6H_5 , in these two classes of compounds may be readily determined by means of this reaction.

The study of this reaction is here extended to isoapiol and propyl isoeugenol, both of which contain the propenyl group, $R-CH=CH-CH_2$, and form dibromides which are readily converted into ketones; the corresponding bromine derivatives of apiol and propyl eugenol do not yield ketones when subjected to an analogous treatment.

It is also shown that the dibromides of certain unsaturated ketones represented by the formula, $R-CH=CH-CO-C_6H_5$, may be readily changed into 1,3-diketones, $R-CO-CH_2-CO-C_6H_5$. The reaction by which these diketones are formed

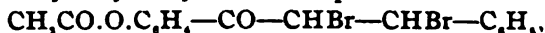
¹ Pond and Beers: *This Journal*, 19, 825.

² Wallach and Pond: *Ber. d. chem. Ges.*, 28, 2714.

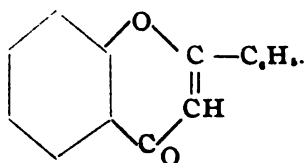
³ Hell and Portmann: *Ibid.*, 28, 2088; Hell and Hollenberg: *Ibid.*, 29, 682.

seems to proceed in much the same manner as in the formation of ketones from propenyl compounds; and there appears to be reasonable ground for the belief that this method of preparing the aromatic β -diketones will prove of certain interest, and perhaps of some value in the study of this interesting class of compounds.

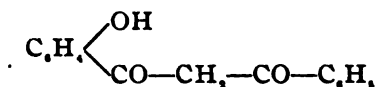
It should be noted in this connection that St. v. Kostanecki in his extended work on the unsaturated ketones obtained flavone and derivatives of flavone by the action of alcoholic potash on the dibromides of certain unsaturated *o*-oxyketones. Thus Feuerstein and St. v. Kostanecki¹ found that alcoholic potash converted 2'-acetyl oxybenzylidene acetophenone dibromide,



into *flavone*,

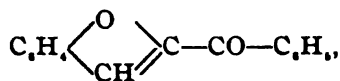


On boiling flavone with a concentrated solution of potassium hydroxide or with sodium alcoholate, it was decomposed into acetophenone, *o*-oxyacetophenone, salicylic acid and benzoic acid, indicating that the first intermediary product of decomposition was the 1,3-diketone, *o*-oxybenzoylacetophenone,



This diketone, however, could not be separated, nor was its presence noted in the formation of flavone from the dibromide of the unsaturated ketone.

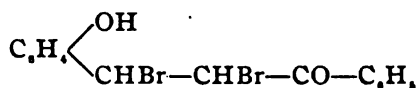
Kostanecki and Tambor² obtained α -cumarylphenyl ketone,



by the action of warm, concentrated alcoholic potash on acetyl-2-oxybenzylidene acetophenone dibromide,

¹ Feuerstein and St. v. Kostanecki: *Ber. d. Chem. Ges.*, 31, 1760.

² Kostanecki and Tambor: *Ibid.*, 29, 237.

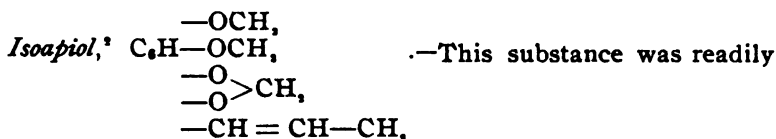


α -Cumarylphenyl ketone decomposes into benzoic acid and cumarone when fused with potash.

These results are therefore quite distinct from those described in this paper.

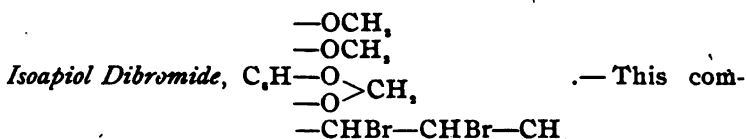
EXPERIMENTAL.

The apiol,¹ $\text{C}_{11}\text{H}_{14}\text{O}_4$, used in our experiments was a very pure specimen, obtained from Schimmel & Co., of Leipzig. It was in the form of fine, white needles, which melted sharply at 30° to 31° and boiled at 294° to 295° .



prepared from apiol according to the method of Eykman,² and Ciamician and Silber³ by heating apiol with an alcoholic potash solution.

Twenty-four grams of apiol were heated with a solution of fifty grams of potassium hydroxide in 250 cc. of alcohol, on a water-bath, for twenty-four hours. The resulting isoapiol was precipitated with a large quantity of water and recrystallized from alcohol. It was obtained in large, white crystals, which melted at 55° to 56° .



pound was prepared by Ciamician and Silber⁴ by adding the theoretical quantity of bromine to a solution of isoapiol in ether, which was cooled to -18° .

Twenty-nine grams (one molecule) of bromine were added

¹ Blanchet and Sell: *Ann. Chem. (Liebig)*, 6, 301; Ciamician and Silber: *Ber. d. chem. Ges.*, 21, 913; Gerichten: *Ibid.*, 9, 1477.

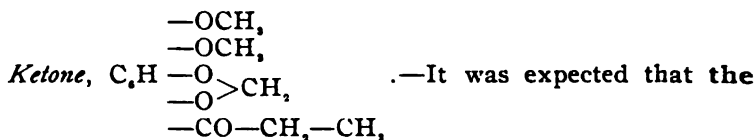
² Ciamician and Silber: *Ber. d. chem. Ges.*, 21, 1621; Ginsberg: *Ibid.*, 21, 1192; Gerichten: *Ibid.*, 9, 1479.

³ Eykman: *Ibid.*, 23, 855.

⁴ Ciamician and Silber: *Ibid.*, 23, 2287.

carefully to a solution of forty grams of isoapiol in 200 cc. of dry ether, well cooled by a mixture of ice and salt. The very slight excess of bromine was at once removed by shaking with sulphurous acid, and, after evaporation of the ether, the resultant oil was dried over sulphuric acid. After standing for about twelve hours the oil solidified to a mass of small, white crystals, which were pressed on a porous plate and crystallized from petroleum ether. It melted at 70° to 72° . It is impossible to obtain this dibromide in a solid form unless the bromine be added very slowly to the ethereal solution of isoapiol, and the resulting, thick oil be carefully dried over sulphuric acid or calcium chloride in a desiccator. It decomposes at once on warming with alcohol, and tends to decompose when crystallized from ordinary solvents, petroleum ether being best adapted for its purification.

Treatment of Isoapiol Dibromide with Sodium Methylate.—Forty-three grams of isoapiol dibromide were added to a solution of ten grams of sodium in 150 cc. of methyl alcohol. A vigorous reaction took place at once with separation of sodium bromide. The reaction was completed by heating the mixture in a flask with a reflux condenser, on a water-bath, for five hours. Water was added to dissolve the sodium bromide, and the solution was acidified with hydrochloric acid, and boiled for two hours to insure the hydrolysis of the unsaturated ether, $R-C(OCH_3)=CH-CH_3$, which is formed by the action of sodium methylate on the dibromide.¹ The dark-red oil which had separated was non-volatile with steam; it was separated by a funnel and allowed to stand for twenty-four hours. At the end of this time, the oil had for the most part solidified; the crystals were filtered by the aid of the pump, and washed with cold ether in which the red oil was very easily soluble, while the crystals were only sparingly soluble. The compound was recrystallized from alcohol, and obtained in white prisms, melting at 95° .



above-mentioned solid, melting at 95° , would prove to be a ketone, since the method of its preparation was analogous to that

¹ Pond and Beers: This Journal, 19, 827.

employed in the preparation of ketones from anethol, isosafrol, etc. The substance was, indeed, readily converted into an oxime, and the latter, in turn, reverted into the ketone by warming with dilute sulphuric acid. This process gave a very pure product which crystallized from alcohol in large, white prisms, melting at 95.5° .

It was found rather difficult to remove a slight red color from the crude ketone unless the oxime was first prepared. This red color is due to a slight admixture of the red oil which is formed together with the ketone.

The pure crystals gave the following results on combustion:

I. 0.1366 gram gave 0.3045 gram carbon dioxide and 0.0692 gram water.

II. 0.1242 gram gave 0.2760 gram carbon dioxide and 0.0664 gram water.

Calculated for			
$\begin{array}{l} -\text{OCH}_3 \\ -\text{OCH}_3 \\ \text{C}_6\text{H}-\text{O}-\text{CH}_3 \\ -\text{O}-\text{CH}_3 \\ -\text{CO}-\text{CH}_2-\text{CH}_3 \end{array}$			
		I.	Found. II.
Carbon.....	60.79	60.50	60.60
Hydrogen.....	5.88	5.66	5.94

$\begin{array}{l} -\text{OCH}_3 \\ -\text{OCH}_3 \\ \text{Oxime, C}_6\text{H}-\text{O}-\text{CH}_3 \\ -\text{O}-\text{CH}_3 \\ -\text{C}(\text{NOH})-\text{CH}_2-\text{CH}_3 \end{array}$
 .—This compound was

very easily prepared by treating six grams of the ketone with an alcoholic solution of hydroxylamine in the usual manner. It crystallizes from methyl alcohol in white needles, which melt at 124° . It is readily changed into the ketone by heating with dilute sulphuric acid on the water-bath for twenty minutes.

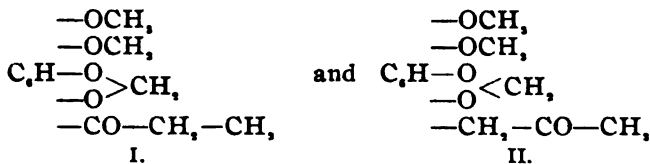
An analysis gave the following results:

I. 0.1513 gram gave 0.3142 gram carbon dioxide and 0.0786 gram water.

II. 0.1420 gram gave 0.2945 gram carbon dioxide and 0.0725 gram water.

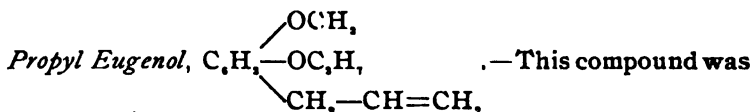
Calculated for			
$\begin{array}{l} -\text{OCH}_3 \\ -\text{OCH}_3 \\ \text{C}_6\text{H}-\text{O}-\text{CH}_3 \\ -\text{O}-\text{CH}_3 \\ -\text{C}(\text{NOH})-\text{CH}_2-\text{CH}_3 \end{array}$			
		I.	Found. II.
Carbon.....	56.91	56.63	56.56
Hydrogen.....	5.93	5.77	5.67

Only two formulas are possible for the ketone obtained from isoapiol; *viz.*,



In order to determine between these two formulas, five grams of the oxime were dissolved in ten cc. of concentrated sulphuric acid and cautiously heated to 250°. The reaction product was diluted with water and distilled with steam. An acid having the odor of a lower fatty acid was obtained in the distillate, separated by the usual method and characterized as propionic acid. This indicates that the ketone has the structure represented by formula I, since a ketone having the formula II could not yield propionic acid by this treatment.

The ketone was reduced in an absolute alcohol solution with sodium, yielding a solid substance; this separated from ether in crystals, which melted sharply at 88° to 89°. It is probably the *alcohol*, $\text{C}_{11}\text{H}_{18}\text{O}_2$, but owing to lack of material no further work could be done with the compound.



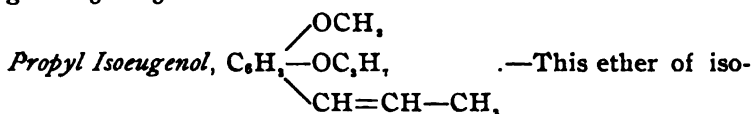
prepared according to the method of Cahours¹ and Wassermann² by heating an alcoholic solution of the potassium salt of eugenol with propyl bromide.

Fifty-seven grams of propyl bromide were added slowly to a hot solution of seventy-five grams of freshly distilled eugenol and twenty-seven grams of potassium hydroxide in 100 cc. of alcohol, and the mixture was heated for two hours on the water-bath. The reaction product was diluted with water and the resultant oil, being non-volatile with steam, was extracted with ether. The ethereal solution was dried with calcium chloride, the ether distilled off, and the propyl eugenol rectified under atmospheric pressure. On redistillation a colorless oil was

¹ Cahours: *Jsb. d. Chem.* (1877), 580; *Ber. d. chem. Ges.*, 10, 237.

² Wassermann: *Ann. Chem.* (Liebig), 179, 375.

obtained, which boiled at 270.5° ; its specific gravity at 15° was 1.0032. Cahours¹ described this substance as a yellow oil, boiling at 263° – 265° .



eugenol containing the propenyl group was produced by heating an alcoholic solution of propyl eugenol with potassium hydroxide. Fifty grams of propyl eugenol, 125 grams of potassium hydroxide, and 250 cc. of alcohol, were heated in the water-bath for twenty-four hours. The reaction-mixture was poured into a large quantity of water, and the resulting solid was filtered, dried, and distilled at the ordinary pressure. It boiled without decomposition at 280° – 281° . The distillate was crystallized from alcohol, and obtained in very large, beautiful, white prisms, which melted at 53° – 54° .

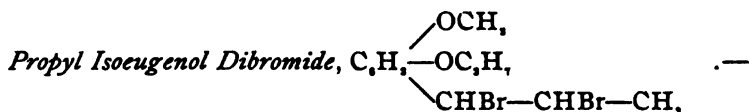
This compound was also readily formed from isoeugenol by heating the potassium salt of the latter in an alcoholic solution with propyl bromide.

Analysis gave the following :

I. 0.1498 gram gave 0.4145 gram carbon dioxide and 0.1170 gram water.

II. 0.1422 gram gave 0.3896 gram carbon dioxide and 0.1098 gram water.

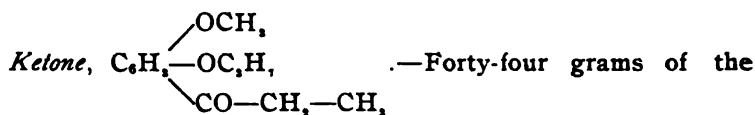
	Calculated for $C_{13}H_{18}O_2$.	I.	Found.	II.
Carbon.....	75.72	75.46		75.48
Hydrogen.....	8.73	8.67		8.57



The dibromide was quantitatively formed by adding the theoretical quantity of bromine to the well-cooled, ethereal solution of propyl isoeugenol. A very slight excess of bromine was removed by agitation with a sulphurous acid solution and the ether allowed to evaporate. No evolution of hydrobromic acid was noticed either during the addition of bromine or on evaporation of the ether. The compound at first formed an oil which

¹ Cahours: *Ber. d. chem. Ges.*, 10, 237.

gradually solidified to a mass of fine, white crystals, melting at 53° – 54° . It is very soluble in alcohol and ether, but cannot be recrystallized without decomposing.



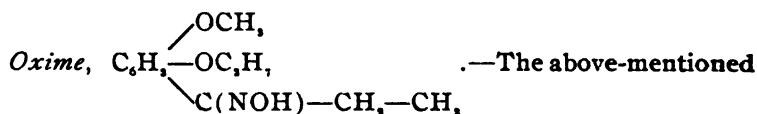
dibromide were added to a solution of eight grams of sodium in 150 cc. of methyl alcohol, and heated on the water-bath for four hours. Water was added, an oil being thrown out, and the mixture was rendered acid with hydrochloric acid and boiled for two hours. On cooling, the oil completely solidified, and was separated, dried, and crystallized from alcohol. It is best obtained in a pure condition by distillation in a vacuum and recrystallization from methyl alcohol. It forms large, splendid prisms, which melt at 63° – 64° and boil with slight decomposition at 284° – 287° under atmospheric pressure. The yield of the ketone from propyl isoeugenol dibromide is quantitative.

The following are the results of the analysis:

I. 0.1316 gram gave 0.3400 gram carbon dioxide and 0.0998 gram water.

II. 0.1303 gram gave 0.3362 gram carbon dioxide and 0.0990 gram water.

	Calculated for $\text{C}_{13}\text{H}_{18}\text{O}_3$.	I.	Found.	II.
Carbon.....	70.27	70.46		70.37
Hydrogen.....	8.10	8.42		8.44



ketone was readily converted into an oxime by treating in the usual manner with hydroxylamine. The oxime separates from alcohol in large crystals, melting at 114° . It is easily reverted into the ketone by warming with dilute sulphuric acid, while concentrated sulphuric acid decomposes it with the formation of propionic acid.

Analysis gave the following results:

I. 0.1380 gram gave 0.3323 gram carbon dioxide and 0.1000 gram water.

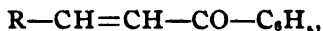
· II. 0.1386 gram gave 0.3334 gram carbon dioxide and 0.1016 gram water.

	Calculated for $C_{13}H_{19}O_2N$.	I.	Found.	II.
Carbon.....	65.82	65.67		65.60
Hydrogen.....	8.01	8.05		8.14

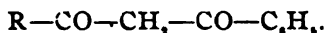
The formation of ketones from isoapiol- and propylisoeugenol-dibromide may be represented by formulas similar to those given in a previous publication.¹ Two molecules of sodium methylate act upon one molecule of the dibromide with elimination of one molecule of hydrobromic acid and production of an unsaturated ether, $R-C(OCH_3)=CH-CH_3$; this ether yields an unsaturated alcohol by hydrolysis with dilute acids, and this in turn suffers a molecular transformation into the isomeric, saturated ketone.

In connection with the study of the action of sodium alcoholate on the dibromides of compounds containing the propenyl group, we thought it of interest to extend our observations to the behavior of the same reagent towards the dibromides of some unsaturated ketones.

Since propenyl compounds, $R-CH=CH-CH_3$, are so readily converted into ketones, $R-CO-CH_2-CH_3$, it seemed probable that unsaturated ketones,



could, by a similar treatment, be changed into diketones of the formula



The results of our experiments on benzylidene acetophenone have fully substantiated this conclusion. Indeed, the reaction takes place so readily, and the yield of the diketone is so large, that this method seems to be especially well adapted to the preparation of this class of compounds.

Benzylidene Acetophenone, $C_6H_5-CH=CH-CO-C_6H_5$.—The benzylidene acetophenone which served as the starting-point of this work was prepared by the method of Claisen and Claparède.¹ Molecular quantities of benzaldehyde and acetophenone were allowed to stand in an alcoholic solution with a small quantity of ten per cent. sodium hydroxide solution. The resulting con-

¹ This Journal, 19, 827.

densation-product separated from ligroin in large crystals, melting at 57° .

Benzylidene Acetophenone Dibromide,¹ $C_6H_5-CHBr-CHBr-CO-C_6H_5$.—This addition-product was obtained by adding one molecular proportion of bromine to the cold ethereal solution of benzylidene acetophenone. It crystallized in small, white prisms, and melted sharply at 156° .

Treatment of the Dibromide with Sodium Methylate.—Twenty grams of benzylidene acetophenone dibromide were heated with a solution of sodium methylate, formed by dissolving three grams of sodium in fifty cc. of methyl alcohol, for three hours, on the water-bath. On completion of the reaction, the sodium bromide was dissolved by the addition of water; a dark-colored oil separated, and the mixture was then acidulated with hydrochloric acid, and boiled for two hours. The oil, which had now assumed a dark red color, was separated from the clear liquid, and after standing for a few hours it solidified to a crystalline mass. This was pressed on a porous plate and crystallized from methyl alcohol, yielding red crystals. These crystals melted at 79° – 80° , but did not appear quite pure. The red color of the crystals could not be removed by repeated crystallization or by boiling with animal charcoal, but when the compound was distilled at ten mm. pressure the distillate solidified at once to a pure, white, crystalline mass. This was crystallized from methyl alcohol and obtained in large, colorless crystals, melting at 80.5° . It is readily soluble in alcohol and ether, and also in sodium and potassium hydroxides; it is precipitated from alkaline solutions by acids. It is insoluble in sodium carbonate. Ferric chloride imparts a dark-violet color to its alcoholic solution. In all its properties the compound agrees with those of dibenzoylmethane, $C_6H_5-CO-CH_2-CO-C_6H_5$, which was first obtained by Baeyer and Perkin,² and has subsequently been investigated by Claisen.³

Analysis gave the following:

I. 0.1257 gram gave 0.3720 gram carbon dioxide and 0.0629 gram water.

¹ Claisen and Claparède: *Ber. d. chem. Ges.*, 14, 2463; see also Kostanecki and Rossbach: *Ibid.*, 29, 1492.

² Baeyer and Perkin: *Ber. d. chem. Ges.*, 16, 2134; Perkin: *J. Chem. Soc.*, 47, 250.

³ Claisen: *Ber. d. chem. Ges.*, 20, 655; *Ann. Chem. (Liebig)*, 291, 83.

II. 0.1278 gram gave 0.3773 gram carbon dioxide and 0.0665 gram water.

	Calculated for (C ₆ H ₅ CO) ₂ CH ₂ .	I.	Found.	II.
Carbon.....	80.35	80.49		80.51
Hydrogen.....	5.35	5.56		5.78

Eight grams of dibenzoyl methane were obtained from twenty grams of benzylidene acetophenone dibromide.

The diketone was further characterized by its conversion into *dibenzoyl-dibromomethane*, C₁₁H₁₀Br₂O₂. This separated from methyl alcohol in white crystals, melting at 95°, and agreed in all respects with the compound obtained by Neufville and Pechmann.¹

The formation of dibenzoyl methane from the dibromide, C₁₁H₁₀O₂Br₂, is probably accomplished by the production of the unsaturated ether, C₆H₅—C(OCH₃)=CH—CO—C₆H₅, which, on hydrolysis with dilute hydrochloric acid, is converted into the unsaturated ketone-alcohol, and then into the diketone.

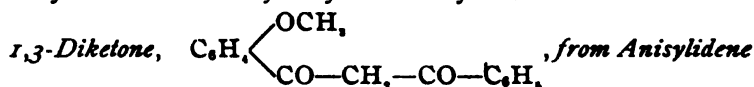
In order to isolate the unsaturated ether, twenty grams of the dibromide were treated as usual with sodium methylate. On the addition of water to the reaction-mixture, a dark oil heavier than water was thrown out; this was separated and dried over calcium chloride. It showed no trace of bromine, and did not solidify after standing for forty-eight hours, or when placed in a freezing-mixture. When a little of the oil was shaken with dilute hydrochloric acid, it immediately became solid, and after crystallization it gave the melting-point of dibenzoyl methane, 80° to 81°. The oil was distilled under 20 mm. pressure, but it came over without a constant boiling-point and suffered considerable decomposition. The distillate did not solidify on standing or after cooling, and was only partially changed into a solid by agitation with dilute acids. Although this oil could not be obtained in a pure condition for analysis, the readiness with which it is converted into the diketone by the action of dilute acids indicates that it contains the unsaturated ether.

A reaction very similar to the above is found in the action of sodium ethylate upon cinnamic ester dibromide. Leighton² found that sodium ethylate acts upon α , β -dibromohydrocinnamic

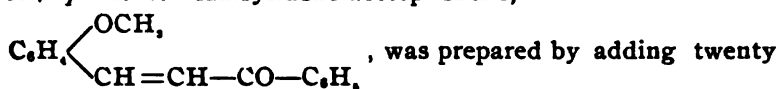
¹ Neufville and Pechmann: *Ber. d. chem. Ges.*, 23, 3377.

² V. L. Leighton: *Am. Chem. J.*, 20, 133.

ester to form β -ethoxycinnamic ester, and the latter yields benzoylacetic acid on hydrolysis with hydrochloric acid.

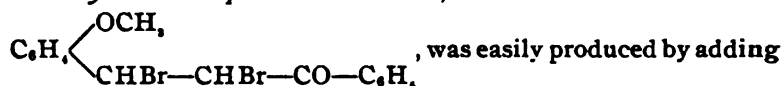


Acetophenone.—Anisylidene acetophenone,



cc. of a ten per cent. solution of sodium hydroxide to a solution of twenty-five grams of anisaldehyde and twenty-two grams of acetophenone in 200 cc. of alcohol. After standing for about eight hours, with an occasional shaking, the condensation-product separated in yellow crystals. It was recrystallized from alcohol and obtained in fine, yellow needles, melting at 77° to 78° .

Anisylidene acetophenone dibromide,



two atoms of bromine to the cold, ethereal solution of the unsaturated ketone. It crystallized from methyl alcohol in small white prisms, and melted at 140° to 141° .

Thirty grams of the dibromide were heated with a solution of five and one-half grams (two atoms) of sodium in 125 cc. of methyl alcohol for three hours. The reaction product was diluted with water, acidified with hydrochloric acid and boiled for two hours. At the end of this time, the dark oil, which had been thrown out on the addition of water, had completely solidified, and was filtered and dried. The substance had a reddish color, and was purified by distillation under diminished pressure, and crystallization from alcohol. It crystallized in white leaflets, which melted at 131° to 132° . It is only sparingly soluble in methyl and ethyl alcohol and ether, but dissolves readily in chloroform and may be precipitated from its solution in this solvent by methyl alcohol. It is very difficultly soluble in sodium hydroxide. Its alcoholic solution is colored an intense reddish violet by ferric chloride.

Analysis gave the following :

I. 0.1410 gram gave 0.3877 gram carbon dioxide and 0.0718 gram water.

	Calculated for $C_{18}H_{14}O_2$.	Found. I.
Carbon	75.58	74.99
Hydrogen	5.51	5.65

This compound, anisoyl benzoyl methane, was also readily formed when sodium ethylate was used instead of methylate. There appeared to be no difference in the yield, but the product was darker colored when ethylate was employed.

Bromine acts upon this diketone with formation of substitution products. When six and one-half grams (two molecules) of bromine were added to a solution of ten grams (one molecule) of the diketone in 150cc. of ether, a vigorous reaction took place with evolution of considerable hydrogen bromide. On evaporation of the ether, a white, crystalline product resulted; this crystallized from methyl alcohol in well-defined white prisms, and melted at 127° to 128° . This compound is probably anisoyl benzoyl dibromomethane, $C_{18}H_{12}O_2Br_2$, and will be further examined.

When piperonal acetophenone dibromide¹ is treated with sodium methylate according to the above-described process, a compound is obtained which crystallizes in small yellow needles, and melts at 86.5° . This substance is at present under investigation.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.
No. 48.]

THE ELECTROLYTIC OXIDATION OF SUCCINIC ACID.

BY CHARLES H. CLARKE AND EDGAR F. SMITH.

Received July 21, 1899.

THE oxidizing action of the current on organic bodies is sure to yield most interesting results. Indeed, the whole organic field remains practically open to investigation along this line. Turn in any direction and ample material will be found for such study. We selected succinic acid as the subject of our investigation. It is, indeed, true that in the past this acid and its salts have engaged the attention of chemists in the electrolytic way, but unfortunately their results are contradictory. No attention was given to the important conditions of current density, voltage, temperature, etc., with the consequence that

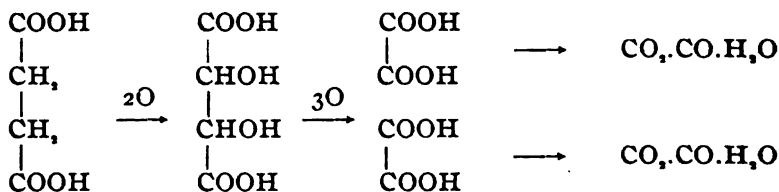
¹ St. v. Kostanecki and Schneider: *Ber. d. chem. Ges.*, 29, 1892.

what has been done electrolytically upon this acid, and, indeed, upon nearly all the acids which have been exposed to the influence of the current, has very little scientific value.

Our aim has been to learn the influence of electrolytic oxygen upon succinic acid. What the products of reduction may be we have not at the present taken pains to ascertain. That is a problem for the future. We have also striven to carefully record the conditions under which we operated and by which our products were produced so that others, if they choose, may repeat and verify them.

The different experiments were conducted in a rather large beaker-glass, using a good porous cup as a diaphragm. The succinic acid was dissolved in definite amounts of sodium hydroxide and known volumes of alcohol. This mixture constituted the anode liquor and it was placed in the porous cup, while the beaker-glass contained sodium hydroxide alone. In those trials in which attention was given to the collection of gases, the mouth of the porous cup was closed with a rubber stopper carrying a small condenser, the latter being suitably connected with a delivery tube leading into an inverted flask or jar, serving as the gasometer.

In considering what the possible result might be in the moderated oxidation of succinic acid, the question naturally arose,—can tartaric acid possibly be produced and then oxalic acid?



Almost every electrolytic study of the acids has made mention of the presence of carbon dioxide, and with us the thought of its possible antecedents was constantly present; hence, we sought to produce and isolate both the tartaric and the oxalic acid.

It may be here remarked that the current used in all the experiments varied from 0.024 to 1.55 ampere for 100 sq. cm. of anode surface. The period of action, as will be seen, ranged from one to ninety-eight hours. When the trial was concluded

the anode liquor had a red color and an aromatic odor. It was acidified with hydrochloric acid, when a great deal of carbon dioxide was evolved. After cooling the liquid was extracted with ether and the watery layer removed by a separatory funnel. Portions both of the ethereal and of the aqueous layers, after the removal of silica and alumina, were carefully freed from other impurities and tested for tartaric acid and oxalic acid. In the first instance recourse was had to the production of the silver mirror, and in the second to the formation of calcium oxalate. The ether extracts of the two experiments showed the mirror, and one of them calcium oxalate. Traces of these acids, therefore, were undoubtedly present. We next endeavored to discover some better means of obtaining and identifying them. During the process of the oxidation, milk of lime was cautiously introduced into the anode chamber. At the expiration of eighteen hours a voluminous precipitate was present. This was filtered out, washed and treated with acetic acid. Much carbon dioxide was evolved, but there remained a precipitate, white in color, which proved to be calcium oxalate. This was then treated with dilute sulphuric acid, filtered and warmed, while potassium permanganate was run into the acid liquid. In this way the presence of 0.0814 gram of oxalic acid was proved.

The coloring-matter of the ethereal extract was isolated. In the purifying process much of it was lost, and the remainder, unfortunately, was also lost through a mishap in making the combustion. The substance, whatever it may prove to be, never appeared in large quantities. It is undoubtedly aromatic in its nature. It melted at 178° , and re-solidified at 169° C.

The gases collected in certain of the oxidations were in the early periods mainly oxygen and carbon monoxide, which later increased in volume and were accompanied by ethylene, methane, and hydrogen.

The appended tables show the working conditions and the corresponding results. To summarize, we may say that the electrolytic oxidation of succinic acid in a divided cell gave *tartaric acid, oxalic acid, some aromatic bodies, oxygen, carbon monoxide, carbon dioxide, ethylene, and methane.*

Experiment number.	Succinic acid. Grams.	Sodium hydroxide. Grams.	Alcohol. cc.	Water. cc.	Time. Hours.	N. D. 100.	Volts.	Temperature. Degrees.	Remarks.
1	2	4	75	—	6	0.465	3.74	62	Trace of reducing substance in ether extract.
2	2	6	75	—	8	0.361	4.19	65.5	
3	22	46	75	100	5	0.505	2.28	63	
4	17	33	—	100	39	0.461	2.10	22	Obtained tar, although no alcohol was present.
5	12	24	50	10	18	0.409	2.90	22	Ether extract did not react with $C_6H_5NHNH_2$.
6	10	20	50	10	21	0.359	3.00	22	
7	5	10	50	10	1	0.177	2.74	22	
8	5	50	50	50	18	0.144	2.37	22	
9	5	50	50	50	65	0.024	1.30	22	Muslin cell.
10	5	50	—	50	24	0.035	2.57	23	" "
11	5	50	—	50	24	0.046	2.55	24	" "
12	5	50	—	50	113	0.049	2.55	23	Trace of oxalic acid in water solution.
13	5	50	50	50	12	1.000	3.52	25	
14	5	35	50	65	19	0.262	2.87	24	Trace of oxalic acid in water solution.
15	5	25	50	50	23	0.287	3.22	27	
16	5	50	50	50	20	1.410	4.93	37	Obtained 0.1046 gram $(COOH)_2 \cdot 2H_2O$.
17	5	50	—	50	47	0.321	2.82	25	Traces of oxalic acid in water solution and ether extract.

¹ Twenty per cent. soda solution used hereafter.

18	5	50	50	100	18	0.420	3.42	29	Obtained 0.0075 gram (COOH) ₂ ·2H ₂ O.
19	5	—	—	—	14	0.685 1.912	1.98	26	Used acetic acid solution of Pb(C ₂ H ₃ O ₂) ₂ with lead electrodes. Negative results.
20	5	50	50	50	37	0.757 1.501	3.57	35	Trace of tartaric acid in ether extract. (See Gas Analysis table.)
21	5	50	—	100	19	1.545	3.27	29	See Gas Analysis table.
22	5	50	—	100	21	1.483	3.50	29	See Gas Analysis table.
23	5	50	50	100	53	0.540	3.58	25	
24	5	50	50	100	65	0.212	2.55	23.5	
25	10	100	50	50	38	0.780	2.88	24	
26	10	100	50	50	29	0.286	4.25	23	See Gas Analysis table.
27	10	100	50	50	39	0.773	3.08	24	
28	10	100	50	50	24	0.064	2.57	22	
29	10	—	50	—	98	0.555	2.00	24	Current varied from 0.038–0.899. Nickel electrodes, muslin cell, no tar.
30	10	100	50	50	24	0.756	2.69	28	
31	10	100	50	50	28	0.357	1.83	26	
32	10	100	75	75	55	0.746	2.89	28	See Gas Analysis table.
33	10	100	75	75	68	0.916	2.59	25	See Gas Analysis table.
34	10	100	100	100	82	0.753	2.91	30	See Gas Analysis table.
35	10	100	50	100	70	0.909	2.03	28	
36	10	40	40	—	48	0.737	3.43	29	Two cells { Outer lost 2.72 NaOH = 14.62 per cent. } Ratio $\frac{1.000}{0.777}$. Middle lost 2.868 NaOH = 11.37 per cent.
37	10	35	35	—	112	0.729	4.30	26	Two cells { Outer lost 6.04 NaOH = 27.55 per cent. } Ratio $\frac{1.000}{0.746}$. Middle lost 7.24 NaOH = 20.57 per cent.

¹ By this is meant that the cup containing the anode liquor was placed within a larger, similar vessel, and the latter in a large beaker containing the cathode solution.

GAS ANALYSES.

Experi- ment number.	Sample number.	Oxygen. Per cent.	Ethylene. Per cent.	Carbon monoxide. Per cent.	Methane. Per cent.	Hydro- gen. Per cent.
20	1	15.6	9.8	1.3	—	—
21	1	18.0	16.0	4.4	—	—
21	2	79.6	—	—	—	—
22	1	66.7	—	1.0	—	—
25	1	17.2	1.0	10.0	—	—
32	1	3.06	1.96	6.55	44.11	17.90
32	2	3.18	2.72	12.84	24.40	35.88
33	1	77.5	—	3.2	—	—
34	1	18.5	—	1.0	—	—
34	2	2.4	3.1	9.5	31.2	28.9
34	3	41.0	1.0	4.0	—	—
36	1	28.2	3.6	—	—	—
36	2	75.4	5.0	9.6	5.00	0.8
36	3	39.4 ¹	14.2	—	—	—
36	4	83.5	7.2	4.3	—	—
37	1	31.0	3.6	3.6	—	—
37	2	60.8	5.8	—	—	—
37	3	66.7	4.6	2.8	—	—
37	4	77.4	2.0	2.6	—	—

NOTES ON THE DETERMINATION OF SULPHUR IN
PIG IRON.

BY M. J. MOORE

Received August 4, 1899.

MUCH has been said regarding the inaccuracy of the volumetric method for the determination of sulphur in pig iron, and many good reasons too well-known to mention here, have been given by way of explanation. I will refer, however, to one article by Phillips² which illumines some of the dark places admirably.

The writer is not aware that any mention has ever been made that physical treatment was responsible for a great portion of the error, such treatment of course, changing the chemical composition of the iron. It is the practice of nearly all if not all, steel and furnace plants to pour the molten metal into water, this being called a "shot sample." The shot thus formed are taken to the laboratory and crushed in a steel mortar and passed

¹ It was found that the pyrogallie acid was exhausted; hence this discrepancy.² This Journal, 17, 891.

through a sixty or eighty mesh sieve, the powder being subsequently analyzed for silicon and sulphur.

I was brought face to face with the sulphur problem some little time ago and in order that the reader may appreciate my plight some explanation will be necessary.

We were called upon to take samples every hour from the cupolas and mixer, analysis being made for silicon and sulphur on each test continuously for the twelve hours. Our practice at this time was to catch a small test in a sand mold, but it was found necessary to change the mode of sampling because the cupola test was nearly always too hard to drill owing to low silicon and high sulphur which rendered the metal white. The mixer tests, however, could be drilled without any trouble. In order to get around this difficulty we caught shot samples from the cupolas but still continued sampling from the mixer in the old way. Continuing this for twenty-four hours and comparing results it was found that the mixer samples carried more sulphur, apparently, than the cupola samples when the reverse should have been the case especially when low sulphur furnace metal was charged into the mixer. So in order to get comparative results shot samples were caught at the mixer. The next problem that presented itself was to find why there was such an apparent increase of sulphur from the mixer metal to the steel.

To ascertain if there was any difference in sulphur when simply the volumetric method was used, between a drilled sample and a shot sample, samples were caught from the mixer ladle while the metal was being poured into the converter. A portion of the metal was poured into water and the balance into a sand mold. The shot samples were reduced in the usual manner and passed through an eighty mesh sieve and the sand samples were drilled. Determinations for sulphur were made on each, both by the volumetric and gravimetric methods, the latter method according to Blair's "Analysis of Iron and Steel." The results are given herewith :

JOLIET WORKS, ILLINOIS STEEL COMPANY.

Analysis of mixer metal for sulphur, showing that the volumetric method does not give all the sulphur, and that the error is greater in shot samples than in drilled samples.

Shot Samples from Mixer.

Date.	Blow No.	Volumetric method.	Gravimetric method.	Difference.	Sulphur in residue.	Volumetric sulphur plus residual.	Column 2 minus column 5.	Sulphur in steel.	Remarks.
1899.		1	2	3	4	5	6		
Jan. 9 ..	1026	0.056	0.081	0.025	0.005	0.061	0.020	0.083	Samples were caught from same test ladle.
" 16 ..	2123	0.064	0.096	0.032	0.008	0.072	0.024	0.103	
" 16 ..	2124	0.067	0.095	0.028	0.007	0.074	0.021	0.104	
" 16 ..	2125	0.070	0.103	0.033	0.008	0.078	0.025	0.106	
" 16 ..	2126	0.073	0.103	0.030	0.006	0.079	0.024	0.106	
Mean ..		0.066	0.096	0.030	0.007	0.073	0.023	0.100	

Sand Samples from Mixer.

Date.		1	2	3	4	5	6		
1899.									
Jan. 9 ..	1026	0.068	0.081	0.013	0.0113	0.079	0.002	0.083	Note difference between the volumetric method in column 1.
" 16 ..	2123	0.089	0.098	0.009	0.007	0.096	0.002	0.103	
" 16 ..	2124	0.087	0.101	0.014	0.009	0.096	0.005	0.104	
" 16 ..	2125	0.087	0.103	0.016	0.008	0.095	0.008	0.106	
" 16 ..	2126	0.088	0.103	0.015	0.005	0.093	0.010	0.106	
Mean ..		0.084	0.097	0.013	0.008	0.092	0.005	0.100	

Referring to the mean results we find in column 1 the difference by the volumetric method to be 0.018. This is enough to condemn the practice of taking shot samples.

In column 2 the total sulphur by the gravimetric method is practically the same in each case. In column 3 one exceeds the other by 0.017. In column 4 the residual sulphur in each case is practically the same and in column 6 we see that all the sulphur under shot samples has been accounted for except 0.023 per cent., while under sand samples we are obliged to account for but 0.005 per cent. Or, in one case there is an actual loss of 23.95 per cent., while in the other but a trifle over five per cent.

The results herein given I consider conservative as both

Messrs. Blair and Dudley have pointed out that all the sulphur is not oxidized by the aqua regia method. The writer feels that too much stress cannot be brought to bear on the sulphur question in pig iron as no concordant results can be brought about from the pig iron to the steel.

One of the prominent eastern mills, to account for the error, uses a factor which is far ahead of reporting 100 per cent. of the results wrong as is the case with the evolution method. In conclusion, the writer earnestly invites any criticism if he has made misstatements. His motive has only been to help along the science.

Note.—Since writing the above more experimenting along this line with iron low in sulphur, say No. 1 Bessemer, has brought out the fact that the error between the gravimetric and volumetric methods is not so apparent until about a No. 2 grade is reached.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE AGRICULTURAL EXPERIMENT STATION.]

A CONTRIBUTION TO THE CHEMISTRY OF BUTTER-FAT.

BY C. A. BROWNE, JR.

Received August 2, 1899.

III. THE CHEMISTRY OF RANCIDITY IN BUTTER-FAT.

THE phenomena attending the development of rancidity in fats have attracted the attention of chemists for many years; even before the beginning of the present century, ere Chevreul had begun his classical "*recherches chimiques sur les corps gras*," and when the chemical constitution of fats was still unknown, it had been surmised that the physical changes which oils and fats underwent on long keeping were simply the results of oxidation; and this is the view most generally accepted at the present time, notwithstanding the fact that many eminent chemists in the past have sought to explain the development of rancidity in other ways.

From the very complexity of its composition we would suppose butter-fat to be a rather unstable body; if butter-fat is sealed up and preserved in a cold, dark place, it will retain its normal character and appearance for many months, but if kept in a

warm locality with free exposure to the air and light, it will very speedily undergo chemical and physical changes and become, as we say, rancid.

By the term "rancidity" is meant not simply, as is generally supposed, a development of free acid (though this is the general concomitant of rancidity), but any chemical or physical change in the character of a fat from the normal. Fats can be rancid without necessarily being very acid;¹ rancidity, according to the present most commonly accepted understanding of the term, is simply oxidation, and in the early stages of the process butter-fat may lose its characteristic color and smell, and develop an abnormal lardy taste, and still not show an excessive degree of acidity.

That rancidity in butter, as many authorities aver, is primarily the result of the activity of bacteria, is no doubt partly true of whole butter with its lactose, casein, and other constituents to serve as bacterial food, but it is certainly not the case with pure butter-fat which is unable to support micro-organic life. The independent researches of both Duclaux² and Ritsert³ prove beyond question that bacteria cannot thrive in a medium of pure fat, and that all changes which take place in fats on keeping are wholly the results of an oxidation, conditioned to a great extent by exposure to light. The distinction between rancid butter and rancid butter-fat should be borne in mind, since the former condition may prevail without the latter. We have paid but little attention to the development of rancidity in whole butter,⁴ and will make this a subject for future study. The present work is confined entirely to those changes which the pure fat undergoes after its separation from all impurities.

¹ We believe v. Klecki was the first to distinguish between the terms rancidity and acidity. *Ztschr. anal. Chem.*, 34, 633 (1895).

² *Annal. de l'Institut Pasteur*, 1888.

³ *Untersuchungen über das Ranzigwerden der Fette*.

⁴ Lactic acid is always found in both fresh and rancid butter, but never in rancid butter-fat. We have found 0.08 per cent. of lactic acid in fresh butter made from ripened cream, and 0.12 per cent. in a rancid butter. The latter sample also contained 0.23 per cent. of free volatile acids, having a mean molecular weight of 94, to which acids the rancid odor and taste of the butter were no doubt largely due.

The statement frequently met with that rancidity in butter is produced by the action of a butyric ferment upon the fat with the formation of butyric acid, is not warranted. It is a well-known fact that milk sugar may pass by fermentation through lactic into butyric acid, and there is every probability that, under favorable conditions, much of the lactose in butter is converted in this way into volatile acid products.

The part which bacteria play in the spoiling of butter has been studied but little up to the present time; the question is one well worth the attention of bacteriologists.

The three factors most active in the production of rancidity in fats are openness to air, exposure to light, and degree of warmth. Given sufficient time, decomposition may occur with the suppression of any one or even two of these elements, but it is of course most rapid when all three conditions are favorable.

In the development of rancidity in butter-fat, under the usual conditions named above, there are observed first of all several changes as regards color, odor, taste, and general appearance. The sample examined begins first to acquire a lighter color; this change appears first on the surface, and the parts most exposed to the light, from which points the action spreads slowly downward until finally the whole mass has become bleached.¹

With this loss of color we notice also the development of a lardy odor and taste; as the period of rancidity advances the odor increases in pungency, while the taste, which at first was not markedly acid, becomes exceedingly burning and unpleasant. In addition to the above we observe some changes in consistency; the sample, which originally was firm and solid in texture, begins to take on a granular look and finally turns, after many months, into a semisolid pasty mass.

If we determine the various constants of a butter-fat at different periods of rancidity, we notice still other important changes, as can be seen from the following table:

TABLE XII.

Age of sample.	Degrees rancidity.	Acid number.	Saponification number.	Ether number.	Reichert number.	Iodine number.	Oleic acid. Per cent.
Fresh	0.9	0.48	228.1	227.6	15.63	34.95	38.79
1 week	2.3	1.28	230.3	229.0	15.80	34.55	38.35
1 month	19.4	10.90	241.0	230.1	17.00	28.40	31.52
2 months	51.5	28.84	260.0	231.2	18.75	14.35	15.93
4 months	53.5	30.00	262.1	232.1	19.80	11.15	12.38
8 months	63.2	35.38	269.3	233.9	21.13	8.55	9.49

We observe with the development of rancidity, a decided increase in the acid, saponification, and Reichert numbers, a slight increase in the ether number, and a very marked decrease in the iodine absorption.

“Degrees rancidity” is a constant employed by many chem-

¹ This observation pertains only to samples of natural color; with butters artificially colored the bleaching is not always evident, showing that certain butter colors are not affected by the development of rancidity.

ists as another way of expressing the free acid in fats, and is placed in this and succeeding tables only for the purpose of comparison. It was introduced into fat analysis by Stockmeier¹ and represents the number of cubic centimeters of normal alkali required to neutralize the free acid in 100 grams of fat: the number of cubic centimeters of tenth normal alkali necessary to neutralize the free acid in ten grams of fat would also give "degrees rancidity;" one degree rancidity would correspond to an acid number of 0.56.

The effects of rancidity upon the composition of butter-fat are also shown by Table XIII, where the chemical constants of four different samples are given in both the fresh and rancid conditions.

TABLE XIII.

Butter-fat.	Condition.	Degrees rancidity.	Acid number.	Saponification number.	Ether number.	Iodine number.	Oleic acid. Per cent.	Acetyl number.	Insoluble acids. Per cent.	Glycerol. Per cent.
1a	Fresh	0.80	0.45	229.9	229.5	33.93	37.66	4.8	87.20	12.54
1b	Rancid	2.18	1.22	232.3	231.1	29.96	33.26	7.6	86.80	12.40
2a	Fresh	0.89	0.50	223.9	223.4	34.49	38.28	3.5	88.96	12.21
2b	{ Rancid, } { 1 month }	12.66	7.09	233.7	226.6	28.69	31.85	10.9	85.06	12.02
3a	Fresh	0.98	0.55	232.6	232.1	29.56	32.81	4.1	86.41	12.69
3b	{ Rancid, } { 2 months }	20.95	11.73	247.7	236.0	19.76	21.93	15.1	80.42	12.35
4a	Fresh	0.93	0.51	225.6	225.1	34.92	38.76	3.8	88.46	12.33
4b	{ Rancid, } { 3 months }	26.43	14.80	245.3	230.5	22.55	25.03	18.0	81.15	11.67

Sample 1 was exposed for three months to air and light in a cold room during winter; *a* represents the unoxidized bottom layer, and was unchanged; *b* represents the upper oxidized part which was bleached and had an abnormal taste and smell. Samples 2b, 3b and 4b were allowed to become rancid in a warm place, with free exposure to air and light.

In addition to the facts previously observed we note from the above table that with the advancement of rancidity there is an increase in the acetyl number and a decrease in the percentages of insoluble acids and glycerol. Other changes produced in the

¹ *Vierteljahrsschrift Nahr. und Genussmittel* (1889), 428. According to Stockmeier, a butter-fat showing more than eight degrees rancidity should be condemned as unfit for use. Chemists have recognized the impossibility of fixing any such arbitrary standard as this: a butter-fat may show only two or three degrees rancidity and still be offensive to our organs of sense, which latter, we may say, are far superior to any chemical methods in forming judgments as to the palatability of foods.

chemical and physical constants of butter-fat by rancidity will be presented in the course of the article.

EFFECTS OF RANCIDITY UPON THE ACIDS OF BUTTER-FAT.

It is a well-known fact, and one wholly confirmed by the preceding tables, that the oleic acid is the constituent of butter-fat most susceptible to chemical change; being an unsaturated compound it absorbs oxygen with great avidity at the points of unsaturation, yielding either oxy-compounds or decomposing into simpler bodies of lower molecular weight. It is impossible to express by chemical equations either of these changes, owing to the complexity of the reaction and the great variety of products formed.

By means of oxidizing agents oleic acid has been found to yield not only all the members of the homologous series from formic to capric acid, but also certain dibasic and oxy-acids.¹ While the oxidation process itself, which takes place with oleic acid in the development of rancidity, is less violent than that produced by artificial means, we may say that the character of the decomposition products is to a considerable extent the same.

A. Scala² detected in a strongly rancid olive-oil formic, acetic, butyric, and oenanthylic acids, also several dibasic acids of the type $C_nH_{m-2}O_4$, among others azelaic and sebacic acids; besides these another acid was isolated which, from the analysis of its barium salt, was identified as dioxystearic acid. The same authority also shows that the saturated acids could take no part in the formation of these decomposition products, since they offer a complete resistance to oxidation; small portions of stearic and palmitic acid, on long standing, were found to suffer under ordinary conditions no change in weight; oleic acid, on the other hand, after ten months' exposure to the air and light, increased in weight over eight per cent. As an additional confirmation of this, it was found that the increase in weight, which different fats underwent on becoming rancid, was in direct proportion to their content in oleic acid.

The amount of oxygen which butter-fats absorb on becoming rancid we have found to vary somewhat with the conditions. A

¹ Watts' Dictionary of Chemistry, Edition of 1892, 3, 637.

² Staz. sperim. agr. ital., p. 613 (1897). Abstract in Biedermann's *Centrbl. für Agriculturchemie*, March, 1899, p. 196.

thin layer of butter-fat, exposed in a melted state to the action of air and light, gained at the end of two weeks 1.54 per cent. of the original weight; it then began to lose, and at the end of two months had lost 1.94 per cent. of the weight of the sample when fresh. Chemical change proceeds much faster with fats if melted, so that the preceding example can not be taken as a fair illustration of what takes place under ordinary conditions.

The following elementary analysis of two butter-fats, one fresh and the other rancid, gives some information as regards the amount of oxygen absorbed during rancidity.

TABLE XIV.

Butter-fat.	Condition.	Carbon. Per cent.	Hydrogen. Per cent.	Oxygen. Per cent.
1	Fresh	75.17	11.72	13.11
2 ¹	Rancid, 2 years old	73.88	11.57	14.55

These results show that the effect of rancidity is to cause a decrease in the percentages of carbon and hydrogen, with a corresponding increase in the percentage of oxygen. Similar results were secured by Lenz² in the case of fresh and rancid horse-fat.

Inasmuch as the iodine number is dependent upon the amount of oleic acid, it is obvious enough that this constant should show a decrease as the period of rancidity advances. We have given in Tables XII and XIII the percentages of oleic acid corresponding to the various iodine numbers. There is some uncertainty among chemists as to the accuracy of calculating the per cent. of oleic acid from the iodine absorption;³ this uncertainty would be still greater in the case of rancid fats, where there is the possibility that other unsaturated compounds besides oleic acid may for the time exist.⁴

The increase in the saponification number as the period of rancidity advances, can be explained only by the breaking up of higher acids into acids of lower molecular weight,—an explanation which is confirmed by the decrease observed in the per-

¹ This sample, which was badly decomposed, stood during the time indicated in a cool place near a window, where the light could have its full effect.

² *Ztschr. anal. Chem.*, p. 441 (1889).

³ For a discussion of this point consult Wiley's *Agricultural Analysis*, 3, 367. See also this Journal, 21, p. 811.

⁴ Such an error would not alter the main facts of the case, however, as the effect would be to magnify rather than diminish the actual percentage of oleic acid.

centage of insoluble acids, and by the increase which takes place in the Reichert number.

It was thought that a determination of the mean molecular weight of the volatile acids from rancid butter-fats would throw some light upon the character of the lower acids formed by decomposition, but the results were in some ways disappointing. The majority of the experiments showed but little difference between the molecular weights of the volatile acids from the fresh and rancid samples, the general tendency seeming to be towards a slight decrease in this constant, as the butter-fat became rancid. The mean molecular weight of the volatile acids formed by decomposition would appear from this to have nearly the same value as that of the volatile acids in the fresh sample; this would bear out the view that, in the breaking up of the oleic acid, several different soluble acids are formed, the lower members of the series apparently being produced in the largest quantity.

The free acid, which soon makes its appearance in all rancid fats, is due not simply to oleic acid and its decomposition products, but to other acids as well. In the development of rancidity there seems to be a gradual breaking up of all the glycerids. Samples of tripalmitin which we have prepared from butter-fat, while much more stable than the parent substance, show after long standing the same tendency to become rancid and develop free acid. This is true of other glycerids as well, the acid part of the molecule splitting off from the glycerol base with the probable disruption of the latter. In the case of complex oleins (oleobutyrim, oleopalmitin, etc.), the changes which so soon effect the oleic acid would no doubt hasten the disintegration of the entire glycerid. The first change which manifests itself in fats on becoming rancid is apparently an oxidation of some oleic acid within the molecule, as changes appear in physical and chemical properties before any considerable development of free acid. Butter-fat No. 1 in Table XIII affords us a good illustration of this; the upper oxidized layer of this sample, when compared with the lower unchanged part, shows a decrease of over four per cent. in oleic acid, and an increase of nearly three units in the acetyl number, while the acid number of the

rancid portion appears but eight-tenths higher than that of the unchanged fat.

A determination of the iodine absorption of the free insoluble acids throws some light upon the proportion of free oleic to other acids. 100 grams of a rancid butter-fat were shaken with an equal quantity of hot ninety-five per cent. alcohol. After cooling completely in ice-water, the alcoholic solution was poured through a filter and exactly neutralized with a dilute solution of potassium hydroxide, using phenolphthalein. The solution was then heated on the steam-bath until all alcohol was evaporated, when the residue was treated with 100 cc. of hot water. The soapy solution, after standing on the bath for a little while to allow any fat which may have been removed by the alcohol to rise, was filtered, cooled and thoroughly extracted with ether to remove all traces of unsaponified matter. An excess of dilute hydrochloric acid was then added to decompose the soaps, and the insoluble acids collected in the usual way.

The iodine number of the free insoluble acids obtained from a rancid butter by this process was 18.47, corresponding to 20.50 per cent. of oleic acid. Thum¹ found in experiments with palm- and olive-oil that the free fatty acids in rancid oils contained oleic acid in almost exactly the same proportions as in the neutral fat. Similar results were obtained by Spaeth² in the case of rancid lards. Such experiments show that the method, so commonly practiced, of calculating the total acidity of rancid fats to oleic acid alone is by no means accurate.

The amount of free volatile or soluble acids in rancid butter-fats is much smaller than might be expected. A comparison of the acid numbers, and the acid numbers for the water-soluble acids alone, indicates that in the early stages of rancidity at least, the free soluble acids bear to the total free acids a relation smaller than that existing between the soluble acids and total acids of normal butter-fat. The following table will make this clearer:

¹ *Ztschr. angew. Chem.*, 482 (1890).

² *Ztschr. anal. Chem.*, 471 (1896).

TABLE XV.

Butter-fat.	Character of sample.	Total acid number (<i>t</i>).	Water soluble acid number (<i>s</i>).	Relation ($\frac{s}{t}$)
1.....	Rancid, 1 month	7.09	0.84	0.1184
2.....	" 2 months	11.73	1.57	0.1338
3.....	" 8 "	35.38	5.99	0.1664
Total acids of butter-fat,		228.5 ¹	40.5 ²	0.1772

The determination of the value *t*, or ordinary acid number, has already been described³ and need not be mentioned here. The value *s*, or water-soluble acid number, represents the milligrams of potassium hydroxide necessary to neutralize the free water-soluble acids in one gram of fat, and is found by washing about ten grams of the rancid fat with successive portions of boiling distilled water until all acid is removed, and then titrating the filtrate with tenth-normal alkali.

It is seen from the preceding table that the value $\frac{s}{t}$ increases with the period of rancidity, and approaches the relation existing between the total and soluble acids of normal butter-fat; this relation would no doubt be equaled or even exceeded by fats in a very advanced stage of rancidity. The results in Table XV confirm the statement of Bondzynski⁴ and Rufi that rancidity in butter-fat is due principally to the formation of free insoluble acids, and that free volatile or soluble acids are not found to any extent except in a very advanced stage of decomposition.⁵ This would not only indicate that the glycerides of the soluble acids in butter-fat are the most stable, but also leads to the following very pertinent question. If the statement previously made in regard to the breaking up of oleic acid into lower soluble acids be correct, *why is it that these acids do not appear to any great extent in the free condition?* That such acids are apparently formed was shown in Table XII by the increase in the Reichert number which fats undergo on becoming rancid, and that they are formed to a considerable extent, seems evident from the decrease which takes place in the percentage of insoluble acids, as is seen from Table XIII.

¹ The average saponification number of butter-fat. This Journal, 21, 613. Table I.

² The milligrams potassium hydroxide required to saponify the soluble acids in one gram average butter-fat. *Ibid.*, p. 628.

³ This Journal, 21, 614.

⁴ *Ztschr. anal. Chem.*, 1 (1890).

⁵ Spaeth found the same true of rancid lard. *Ibid.*, 479 (1896).

There are several possible ways of explaining this non-appearance of the soluble acids formed by decomposition. There is the possibility that the oleic acid, when in the glyceride form, may split up into a soluble and an insoluble acid, the soluble acid remaining in combination with the glycerol base; this hypothesis, however, does not seem a tenable one since a large amount of free oleic acid is found in rancid fats, as was shown by a preceding experiment.¹ There is also the possibility that esters of the soluble acids may in some way be formed, but this view seems no more plausible than the other; such esters have been found in whole butter,² but we have not been able to detect their presence in rancid fats.

The best explanation of this difficulty which we have been able to arrive at is the following: the first products formed by the decomposition of oleic acid are not of an *acid* but of an *aldehyde* nature; these aldehyde bodies are further changed by oxidation into soluble acids, but this takes place only in a very advanced stage of rancidity, which would explain the fact, already referred to, that free soluble acids are not formed to any great extent except in rancid fats of considerable age. By the action of alcoholic potash, aldehydes are decomposed into acids, and small quantities of dark resinous compounds;³ this would account for the fact that the soluble acids of decomposition do not appear until after saponification, and would also explain the brown coloration which all rancid fats undergo when treated with alkalis.

The presence of aldehydes in rancid fats is indicated on other than theoretical grounds. The cocoanut-like odor, so peculiar to butter-fat in the early stages of rancidity, and the very pungent smell developed later, are probably due to aldehyde products. Spaeth⁴ has called attention to the reducing action which all rancid fats have on Becchi's silver solution as an evidence of these bodies, while E. von Raumer⁵ has detected their presence by the aid of Schiff's reagent. The latter test we have found to be one of extreme delicacy.

¹ This article, p. 982. Indications are that most of the changes which affect the oleic acid take place after the latter has been set free.

² Amthor: *Ztschr. anal. Chem.*, 10 (1899).

³ Watts' Dictionary of Chemistry, second edition, 1, 111.

⁴ *Ztschr. anal. Chem.*, 487 (1896).

⁵ *Ibid.*, p. 487.

Schiff's reagent is prepared by saturating a solution of rosaniline acetate with sulphur dioxide gas, and allowing it to stand in a stoppered bottle until completely decolorized. In making the test about one cc. of the melted fat is placed in a test-tube with ten cc. of hot water and thoroughly shaken; one cc. of the reagent is then added and the contents of the tube shaken up a second time. If aldehydes are present the fat and liquid underneath will be colored a splendid violet,—the intensity of the coloration being proportional to the rancidity of the sample. Fresh butter-fat gives no test with Schiff's reagent, even after many hours' standing; with fats of moderate rancidity the coloration varies from a pink to a bright cherry-red, while with very old and rancid specimens the layer of melted fat is colored a very dark purple, the liquid underneath being a deep violet. The fact that both fat and liquid were colored would show that aldehydes were present in both soluble and insoluble forms. After saponifying a rancid fat and decomposing the soap solution with an excess of hydrochloric acid, the Schiff test was applied with negative results,¹ thus proving beyond all doubt that the action of alkalies is to completely destroy all compounds of an aldehyde nature.

The existence of aldehydes in rancid fats, and their behavior with saponifying agents, explains another point which we have not yet referred to in connection with Tables XII and XIII. It will be seen from these tables that with the development of rancidity there is a noticeable, but not excessive, increase in the ether number. The true ether number of a rancid fat, representing as it does the milligrams of potassium hydroxide necessary to saponify the neutral fat in one gram of substance, would naturally be lower than that of a fresh sample, since with the breaking up of the glycerides the quantity of neutral fat becomes steadily less.² The presence of aldehydes, however, causes a vitiation in the true ether number; these bodies are not affected in the determination of the acid number, but when the alcoholic potash is added in excess for the determination of the saponification number, the aldehydes, as has been shown, are decom-

¹ The insoluble acids were slightly tinged, but strange to say the coloration was not as pronounced as with the acids from fresh butter-fat. We attribute this reaction in the insoluble acids to a slight decomposition of the oleic acid subsequent to the saponification.

² This supposition is confirmed by the decrease which takes place in the percentage of glycerol.

posed into acids, to neutralize which an excess of potassium hydroxide is required greater than that necessary to saponify the neutral fat alone. This vitiation of the ether number is much greater than the tables indicate, owing to the fact just mentioned that the true ether number of a fat steadily decreases with the advancement of rancidity.

We have already alluded to the fact that oxy-acids are found in all butter-fats irrespective of age, and the statement was made in a previous article that the low acetyl number, which fresh butter-fat shows, and the steady increase of this constant with age, suggest that these compounds are entirely after-products, and do not exist in the milk-fat before secretion. Experiments already mentioned¹ indicate that the oxy-acids are derived entirely from oleic acid, dioxystearic acid being principally formed.

The following table, compiled from results given in Tables XII and XIII, offers a few interesting comparisons, and gives some idea of the probable manner in which the oleic acid of butter-fat is decomposed.

TABLE XVI.

Butter-fat.	Condition.	Oleic acid. Per cent.	Insoluble acids. Per cent.	Loss in oleic acid. Per cent.	Loss in insoluble acids. Per cent.	Acetyl number.	Increase in acetyl number.	Increase in oxy- acids. Per cent. ²
No. 1..	Fresh	38.28	88.96			3.5		
No. 1..	Rancid	31.85	85.06	6.43	3.90	10.9	7.4	1.78
No. 2..	Fresh	32.81	86.41			4.1		
No. 2..	Rancid	21.93	80.42	10.88	5.99	15.1	11.0	2.51
No. 3..	Fresh	38.76	88.46			3.8		
No. 3..	Rancid	25.03	81.15	13.73	7.31	18.0	14.2	3.28
No. 4..	Fresh	38.79	87.72					
No. 4..	Rancid	9.49	72.03	29.30	15.69			

We observe from the above table that the loss in insoluble acids accounts for but little more than half the loss in oleic acid ; the ratio seems to be a fairly constant one, and averages about fifty-five per cent. This figure, then, may be taken to represent approximately the amount of oleic acid in the loss which is con-

¹ By Scala, this article, p. 979.

² Calculated as dioxystearic acid by the formula, $x = \frac{100 \text{ cm.}}{a(56100 - 42x)}$. This Journal, 21, 817.

verted into lower soluble acids.¹ Calculating the increase in the acetyl numbers to dioxystearic acid will make up about twenty-five per cent. more of this loss in oleic acid, thus leaving about twenty per cent. still unaccounted for; the formation of insoluble aldehyde products² during the saponification may explain this discrepancy.

Owing to the formation of oxy-acids the chemical and physical characteristics of the insoluble acids from butter-fat suffer marked changes with the development of rancidity. The following constants were determined on the insoluble acids of butter-fat No. 4 in the preceding table.

TABLE XVII.

Condition of butter-fat.	Mean molecular weight of insoluble acids.	Melting-point of insoluble acids.
Fresh.....	260.2	40.2° C.
Rancid.....	273.7	44.7° C.

These differences are such as one would expect; the increase in the mean molecular weight and melting-point of the insoluble acids, both being the results of the formation of oxy-acids.

EFFECTS OF RANCIDITY UPON THE GLYCEROL OF BUTTER-FAT.

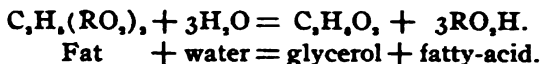
One of the most disputed points in connection with the rancidity of fats is that concerning glycerol. A large number of chemists hold that, as fats become rancid, glycerol is liberated in the free state, and cite the instance of palm-oil, which seems to split up almost quantitatively into its fatty acids and glycerol; in contradistinction to this many chemists, having tested rancid fats for free glycerol with totally negative results, claim that no free glycerol is formed; other chemists, attempting to reconcile these conflicting views, take the somewhat intermediary position, that fats on becoming rancid are decomposed into free acid, and free glycerol, but that the latter is almost immediately destroyed by oxidation.

A quantitative decomposition of a perfectly pure and dry neutral fat into its glycerol and acids, is manifestly impossible, as

¹ Including those already existing and those formed by the action of alkali on the aldehydes.

² The presence of aldehyde condensation products, resin, etc., which are always formed by alcoholic potash, would produce an error in the determination of the insoluble acids. The insoluble acids from rancid butter-fats are invariably colored by these bodies, the coloration varying from a yellow to a dark brown according to the rancidity of the sample.

such a reaction would require the presence of a large amount of water.



To reason from the analogy of palm-oil is not permissible; this oil is abnormal in many ways, containing, as it does, some twelve per cent. of free acid, even when fresh, with a considerable amount of moisture and other impurities.¹

The percentage of glycerol in rancid fats cannot be calculated from the ether number, owing to the vitiation in this constant previously referred to. The process of separating the glycerol from other bodies, and determining its percentage by direct weighing, is never accurate and would be still less applicable with rancid fats, where the glycerol would be contaminated with various impurities. A statement made by some chemists that fats undergo an increase in the percentage of glycerol on becoming rancid, is undoubtedly due to some such faulty method of analysis as the above.

The determinations of glycerol in rancid fat made by us were all performed according to the method of Benedikt and Zsigmondy, as previously described.¹ The results, which are tabulated in Table XIII, all show a decrease in the percentage of glycerol as the butter-fat became rancid, the decrease being proportional to the rancidity of the sample.

It is impossible to say just how this loss of glycerol is incurred; it no doubt takes place in the separation of the various fatty acids, and there is good reason to suppose that these acids, since they do not occur as anhydrides, have seized upon the glycerol radical for the elements of water necessary to their formation. If this theory be correct, very little if any glycerol would appear in the free condition; we have examined rancid butter-fats for free glycerol by washing with large quantities of boiling water, and testing the filtrate by the Benedikt and Zsigmondy method. Small quantities of oxalic acid were formed, equivalent to from one-tenth to two-tenths per cent. glycerol; this may have been derived, however, from the oxidation of water-soluble aldehydes, as well as from glycerol. We believe a small amount of acrolein

¹ According to Benedikt the percentage of impurities with different grades of palm-oil ranges from 0.50 to 17.00 per cent. *Analyse der Fette*, third edition, p. 525.

² This Journal, *21*, 621.

is formed from glycerol in the development of rancidity and attribute the pungent irritable odor which all rancid fats give off—especially on being warmed—to the presence of this compound.

EFFECTS OF RANCIDITY UPON THE PHYSICAL CONSTANTS OF BUTTER-FAT.

The alterations in chemical composition, which butter-fats undergo with age, produce very decided changes upon the physical constants.

It is a well-recognized fact that as rancidity is developed the specific gravity of fats increase. The specific gravity $_{15.5}^{40}$ C. of fresh butter-fat was found to range from 0.9050 to 0.9102; the values of this constant for rancid butter-fats, at the same temperatures of comparison, were considerably higher, and varied between 0.9195 and 0.9252. This increase is easily explained by the fact that in the development of rancidity the oleic acid, of low specific gravity, is changed by oxidation into compounds of greater density. This is in full agreement with the statement of Brühl¹ that "by the addition of oxygen the specific gravity of bodies always exhibits a marked increase, no matter what the product of oxidation may be, whether acid, alcohol, oxy-acid, or other in character." It is owing to this increase in specific gravity that the viscosity of fats becomes greater, as the period of rancidity advances.

In regard to melting-point rancid butter-fats exhibit the greatest irregularity, and we have finally come to the conclusion that it is impossible to make a satisfactory determination of the melting-point of butter-fats in a very advanced stage of decomposition. In the early period of rancidity the melting-point is somewhat higher than that of the fresh butter-fat; the increase, which is probably due to the formation of oxy-compounds of higher melting-point, is not a marked one, however, the differences ranging from 0.1° to 1.5° C. A quite characteristic phenomenon, observed with some rancid butter-fats, was that of double melting-point. As an example a rancid butter-fat, by the capillary tube method,² melted at 24.2° C.; after keeping the

¹ *Ann. Chem.* (Liebig), 211, 128. See note 2, p. 992 of this article.

² The official method could not be used with any degree of success, owing to the solubility of decomposition products in alcohol.

temperature at this point for a few minutes the fat solidified again and, on increasing the heat, remelted at $33.4^{\circ}\text{C}.$ ¹ Samples of excessive rancidity do not exhibit this trait; such fats will usually begin to liquefy at from 22° to $24^{\circ}\text{C}.$, but will remain turbid from insoluble particles, and will not become perfectly clear until the temperature reaches 35° to $40^{\circ}\text{C}.$ This behavior is probably due to the presence of two classes of decomposition products; those of low melting-point, such as fatty aldehydes and lower acids, and those of high melting-point, such as oxy-acids. In this way too would be explained the peculiar semi-fluid consistency, which very rancid fats acquire, fresh butter-fat, under the same conditions, remaining firm and solid.

The development of free acid, which takes place in rancid fats, has a very marked effect upon the critical temperature of dissolution. This simple test devised by Crismer² is especially valuable in testing fats and merits a brief description in this connection. About one-half cc. of melted butter-fat is placed in a slender test-tube with twice its volume of absolute alcohol. The tube is closed with a cork, through which a thermometer is passed so that its bulb is entirely covered with the solution and does not touch the walls of the tube. The tube and thermometer thus prepared are passed through a tightly fitting cork into a larger tube partly filled with water; the whole is then gently heated, with constant shaking, until the mixture of alcohol and butter-fat becomes perfectly clear. The temperature at which turbidity appears, after allowing the apparatus to cool, is noted as the critical temperature.

Crismer has observed that with rancid butter-fats the critical temperature is materially lowered, and that this lowering is proportional to the acidity of the fat. By neutralizing such products with weak alkali and washing the fat with hot water, the normal critical temperature was found to be restored; we have secured the same result by washing the rancid fat with alcohol.

The mean critical temperature of several fresh butter-fats, examined by us according to the above method, was $57^{\circ}\text{C}.$;³

¹ Other instances are known of fatty bodies showing double melting-point. Palmitin melts at $50.5^{\circ}\text{C}.$ and again at $66.5^{\circ}\text{C}.$ *Analyse der Fette*, third edition, p. 44.

² *Bull. Assoc. belge.* 10, 312 (1896). Abstract in *Analyst*, 22, 252, 71.

³ Of the various rapid tests for adulterated butters this is one of the most reliable. Crismer found for pure butter-fat critical temperatures ranging from 50° to $57^{\circ}\text{C}.$, and for margarine and mixtures results between 64° and $78^{\circ}\text{C}.$

rancid butter-fats gave results ranging from 45° to 50° C. according to the degree of acidity.

It is very interesting to note the effect which rancidity has upon the refractive power of fats. All observers¹ agree in this that the refractive index of a fat increases with the development of rancidity, but differ as to the explanation of the phenomenon.

Unfortunately we had no refractometer in the early stages of our work, and so no comparative readings could be made on the various rancid butter-fats used in these experiments. Recently, however, we have been able to make a large number of refractometer readings on various fresh and rancid butter-fats, and in all cases found that the rancid samples gave a higher refractive index. The readings were made on a Pulfrich instrument, the yellow sodium ray (*D*) being used.

TABLE XVIII.

	Range in refractive indices, 30°C.		Mean.
Fresh butter-fats.....	1.45872	1.45922	1.45897
Rancid " "	1.45982	1.45992	1.45987

Instead of using the refractive index as a means of comparison, we have preferred to use the specific refractive power. The coefficient of refraction varies greatly with the specific gravity, so that a determination simply of the refractive index leaves one very much in doubt as to whether or not any changes observed may not be due wholly to differences in density.

The specific refractive power is calculated from the formula² $\frac{N-1}{D}$, in which *N* equals the refractive index of the substance and *D* its specific gravity.

TABLE XIX.

	Specific 30° C (<i>D</i>). gravity 15.5°	Refractive index 30° C (<i>N</i>).	Specific refrac- tive power $\left(\frac{N-1}{D}\right)$.
Fresh butter-fat.....	0.91260	1.45897	0.50292
Rancid " "	0.92571	1.45987	0.49677

It is seen that the specific gravity and refractive index of rancid butter-fats is higher, but that the specific refractive power is lower. These results are in perfect accordance with the

¹ See articles by Spaeth and Scala already referred to.

² Landolt : *Ber. d. chem. Ges.*, 15, 1031.

observations of Brühl,¹ that by the addition of oxygen the specific gravity of bodies shows a marked increase and that the same change takes place but to a less degree with the refractive index, but that the specific refractive power is always *smaller* in the body richer in oxygen.²

In view of this, since the percentage of oxygen increases in fats as they become rancid, the changes which affect the refractive power find an adequate explanation.

Another important effect of rancidity upon fats is the marked decrease in the calories of combustion. This is a fact which requires but little explanation. Rancidity is in reality only a slow process of combustion, like other forms of oxidation; it is therefore plain that a certain amount of heat is given off by fats in the development of rancidity and that in consequence thereof the original heat-producing power must suffer a decrease.³ The following experiments performed on a fresh and rancid butter-fat will illustrate this. A Hempel-Atwater bomb calorimeter⁴ was used in the work.

TABLE XX.

	Chemical composition.			Calories.
	C. Per cent.	H. Per cent.	O. Per cent.	
Fresh butter-fat.....	75.17	11.72	13.11	9366.
Rancid " "	73.88	11.57	14.55	9095.

CONCLUSION.

We have attempted to give in the preceding pages a few of the main facts in connection with the subject of rancidity. The point was made in the beginning of this paper that the nature of the chemical and physical changes, which take place in the decomposition of fats, is one largely dependent upon conditions.

¹ Die chemische Constitution organischer Körper in Beziehung zu deren physikalischen Eigenschaften. By J. W. Brühl. *Ann. Chem.* (Liebig), 211, 121.

² More fully expressed in the language of the original. *Ibid.*, p. 128. "Aus dieser Tabelle ergiebt sich, dass durch die Addition von Sauerstoff die Dichte der Körper stets sehr bedeutend zunimmt, gleichgiltig, welche Art von Verbindung, ob Säure, Alkohol, Oxyssäure, u. s. w., hierdurch gebildet wird. Gleichzeitig, aber weit schwächer, wächst auch der Brechungsindex. Dagegen ist die auf gleiche Dichte reducirte brechende Kraft, oder das Brechungsvermögen, bei dem an Sauerstoff reicheren Körper stets kleiner."

³ Brühl: *Op. cit. supra*, p. 126. "Die Verbrennungswärme der Körper sinkt sowohl durch Vereinigung derselben mit Sauerstoff, * * * * *, oder durch Ersetzung von Wasserstoff durch Sauerstoff."

⁴ Seventh report of the Storrs Agricultural Experiment Station, Conn., p. 135.

The results of the present article were obtained under only one particular set of conditions; *vis.*, those most favorable to the production of chemical change. Had the conditions of warmth, light, and exposure to the air been varied, a difference no doubt would have been observed in the degree and character of some of the changes produced. Further investigations as to these points are greatly to be desired.

As we found it difficult to make the distinction between normal and abnormal butter-fats a sharp one, so are we perplexed if we try to draw the line between the qualities fresh and rancid. Butter-fat, as fresh as it can possibly be obtained, gives distinct acid and acetyl numbers, and these changes were no doubt initiated before the cream was separated and churned; we may say therefore that, in a certain chemical sense, fresh butter-fat itself is rancid. If chemical changes begin thus early, we naturally ask ourselves, to what limits can this process of decomposition in fats go? This is a difficult question to answer for we know of no instances where fats were kept a sufficient length of time to enable any conclusions as to this point being formed. The ultimate products of oxidation would of course be water and carbon dioxide, but under ordinary conditions this result would hardly be reached; we are probably safe in saying that chemical change will not cease until all the glycerides are decomposed and the oleic acid is completely changed; whether or not other changes of a different order, such as the formation of paraffin bodies, may set in, is wholly a matter of conjecture.

Owing to lack of time we were unable to make a closer study of the various decomposition products formed in butter-fat by rancidity; nothing whatever was done toward the separation and identification of the various aldehydes, acids and other bodies produced in rancid fats, and this we feel to be a serious omission to completeness. As we stated at the beginning, these studies upon butter-fat were conducted in a very desultory manner, being pursued only as other laboratory duties permitted; this we offer as an excuse for the very general and fragmentary character of much of our work. We hope if possible in the future to make further studies in this most fascinating field of chemical research.

In conclusion the writer desires to acknowledge the help and encouragement received from various friends. Our thanks are

due to Dr. W. Frear of this experiment station for advice and suggestions in the preparation of these papers; to Dr. G. G. Pond of the Pennsylvania State College for the use of a refractometer, and to Dr. F. E. Tuttle of the same institution for assistance in making combustions; also to Mr. C. W. Norris of this experiment station, who made many of the determinations of specific gravity and melting-point contained in the tables of these articles, and who also rendered valuable assistance in determining calories of combustion. We also wish to express our indebtedness to Messrs. A. N. Diehl and C. P. Beistle of this station for their kindly aid at various stages of the laboratory work.

[CONTRIBUTION FROM THE CHEMICAL DIVISION, UNITED STATES DEPARTMENT OF AGRICULTURE, No. 35.]

SOME BOILING-POINT CURVES.

PAPER II.

J. K. HAYWOOD.

Received July 10, 1899.

In a recent paper on boiling-point curves¹ I presented the results of my work on mixtures of organic liquids in which alcohol, acetone and chloroform respectively was one of the constituents. In the following paper I have worked out the curves for mixtures in which benzene and methyl alcohol, respectively, is one of the constituents.

The apparatus and thermometer used were the same as those employed in my previous work and, therefore, need no description. All of the chemicals used were purified as I have already described, with the addition of benzene, which was first allowed to stand over sulphuric acid to both dry and remove any possible traces of thiophene and then decanted and distilled through a high column. None of the purified materials varied more than 0.5°C . in their boiling-point and nearly all not more than 0.1°C .

All readings were made at the prevailing atmospheric pressure and in no case was the variation great enough to seriously affect the accuracy of the results. For purposes of comparison the curve for benzene and alcohol by Thayer,² for benzene and carbon

¹ *J. Phys. Chem.*, 3, 317 (1899).

² *Ibid.*, 2, 382 (1898).

disulphide by Carveth,¹ for methyl alcohol and acetone and methyl alcohol and chloroform by myself, are included.

Following are the analytical data and charts, in which the temperatures are plotted as ordinates and the percentage compositions by weight as abscissas:

BENZENE AND CHLOROFORM.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.3	761.5	45.2	72.65	761.5
85.1	78.85	761.5	40.5	71.7	761.4
70.4	76.9 ^o	761.5	34.1	70.35	761.4
61.9	75.65	761.5	27.7	68.9	761.4
55.9	74.6	761.5	18.8	66.7	761.4
52.0	73.9 ^o	761.5	8.2	63.9	761.4
47.3	73.025	761.4	0.0	61.6	761.4

BENZENE AND CARBON TETRACHLORIDE.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.35	763.1	45.5	78.3	763.6
82.1	79.8	763.1	40.2	78.1	763.6
73.5	79.4	763.1	35.2	77.9	763.6
66.1	79.15	763.1	28.6	77.65	763.6
59.4	78.9	763.0	19.7	77.35	763.6
51.9	78.6	763.0	10.7	77.1	763.6
47.7	78.4	763.0	0.0	76.925	763.7

BENZENE AND ETHER.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.3	762.9	46.4	47.8	760.7
83.2	67.5	762.9	41.4	46.1	760.7
72.8	60.65	762.9	36.0	44.35	760.8
64.3	55.95	762.7	29.3	42.3	760.9
56.1	52.0	762.4	14.4	38.15	761.0
51.4	50.05	762.0	0.0	34.75	761.1
47.4	48.5	762.0

BENZENE AND ACETONE.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.5	767.2	49.8	62.0	766.5
87.1	72.2	767.1	47.2	61.6	766.5
78.2	68.55	767.0	41.1	60.75	766.6
68.9	65.85	76.70	33.6	59.8	766.6
60.2	63.9	76.70	23.8	58.75	766.6
54.3	62.8	767.0	9.9	57.5	766.6
50.3	62.1	767.0	0.0	56.7	766.7

¹ *J. Phys. Chem.*, 3, 193 (1899).

BENZENE AND METHYL ALCOHOL.

Per cent. benzene.	Temperature.	Barometer.	Per cent. benzene.	Temperature.	Barometer.
100.	80.25	760.8	56.8	58.3	760.5
92.7	60.95	760.8	51.4	58.4	760.5
89.7	59.85	760.8	49.3	58.42	760.4
87.5	59.4	760.8	46.8	58.45	759.5
83.4	58.92	760.8	42.5	58.6	759.5
81.2	58.8	760.8	35.3	59.0	759.6
76.2	58.525	760.8	26.3	59.8	759.7
73.9	58.475	760.8	16.5	61.2	759.8
69.7	58.4	760.8	6.9	63.2	759.8
65.7	58.3	760.8	0.0	65.0	759.9
61.8	58.3	760.7

METHYL ALCOHOL AND ETHYL ALCOHOL.

Per cent. methyl alcohol.	Temperature.	Barometer.	Per cent. methyl alcohol.	Temperature.	Barometer.
100.	65.1	762.7	46.0	70.65	762.5
88.1	66.1	762.7	42.4	71.15	762.5
74.6	67.35	762.7	36.5	72.0	762.5
65.4	68.3	762.7	24.9	73.9	762.5
55.9	69.4	762.7	11.1	76.5	762.5
50.0	70.1	762.7	0.0	78.75	762.5
46.2	70.6	762.7

METHYL ALCOHOL AND CARBON TETRACHLORIDE.

Per cent. methyl alcohol.	Temperature.	Barometer.	Per cent. methyl alcohol.	Temperature.	Barometer.
100.	65.2	765.1	40.6	56.6	765.3
93.9	64.0	765.1	38.5	56.475	765.5
87.2	62.7	765.1	31.8	56.2	765.5
75.0	60.5	765.2	24.9	56.0	765.5
64.0	58.85	765.2	20.7	55.97	765.5
59.6	58.3	765.3	18.4	55.95	765.5
54.9	57.8	765.3	15.0	56.0	765.5
51.6	57.45	765.4	11.1	56.1	765.3
48.6	57.2	765.4	7.4	56.35	765.3
45.6	56.9	765.4	5.9	56.6	765.3
42.1	56.7	765.4	0.0	77.2	765.3

METHYL ALCOHOL AND ETHER.

Per cent. methyl alcohol.	Temperature.	Barometer.	Per cent. methyl alcohol.	Temperature.	Barometer.
100.	65.15	765.3	39.1	40.1	765.3
85.3	57.7	765.3	36.5	39.55	765.3
70.4	50.2	765.3	36.2	39.42	765.3
63.1	47.1	765.3	30.7	38.5	765.1
56.2	44.7	765.3	18.4	36.6	765.1
49.7	42.7	765.3	0.0	34.85	765.1
44.5	41.4	765.3

Chart I represents the results obtained in mixtures where benzene was one constituent. The curve for carbon tetrachloride has already been worked out by Lehfelt,¹ by measuring the vapor-pressure with varying composition, the temperature being kept constant. Since it rested on so few measurements, however, I have thought it worth while to repeat his work. The results obtained were very much the same as those already given by Lehfelt. The curve has no maximum or minimum point and presents no unusual features other than the absence of such a point when the boiling-point of the constituents lie so close together.

The curves for chloroform, acetone, carbon disulphide and ether have neither maximum nor minimum point and present no unusual features. The curve for methyl alcohol, like that for ethyl alcohol, has a minimum point at about 58.3°C . Owing to the flatness of the curve at this point, however, the exact composition of the constant boiling mixture can not be given from my work. We can only say that it lies somewhere between 53 and 67 per cent. of benzene. The methyl alcohol curve cuts the ether curve at a composition of about sixty-nine per cent. benzene, the carbon disulphide curve at a composition of about fifty-five per cent. benzene, the acetone curve at a composition of about thirty-one per cent. benzene, and the chloroform curve at a composition of about six per cent. benzene.

In Chart II the results are given for mixtures of the various liquids with methyl alcohol. The curve for ethyl alcohol has neither maximum nor minimum point, which we might expect since the boiling-points of these two liquids are rather close together. But, here again, as in the carbon tetrachloride and chloroform curve, presented in my first paper, the close chemical relationship of these two compounds may be a strong modifying influence.

The curve for benzene has a minimum point at about 58.3°C . and a composition of fifty-three to sixty-seven per cent. benzene. The curve for carbon tetrachloride has a minimum point at about 55.95°C . and a composition of 18.4 per cent. methyl alcohol. The curve for ether has neither maximum nor minimum point and presents no unusual features. The curves for chloroform

¹ *Phil. Mag.*, and *J. of Science*, 46, No. 278 (1898).

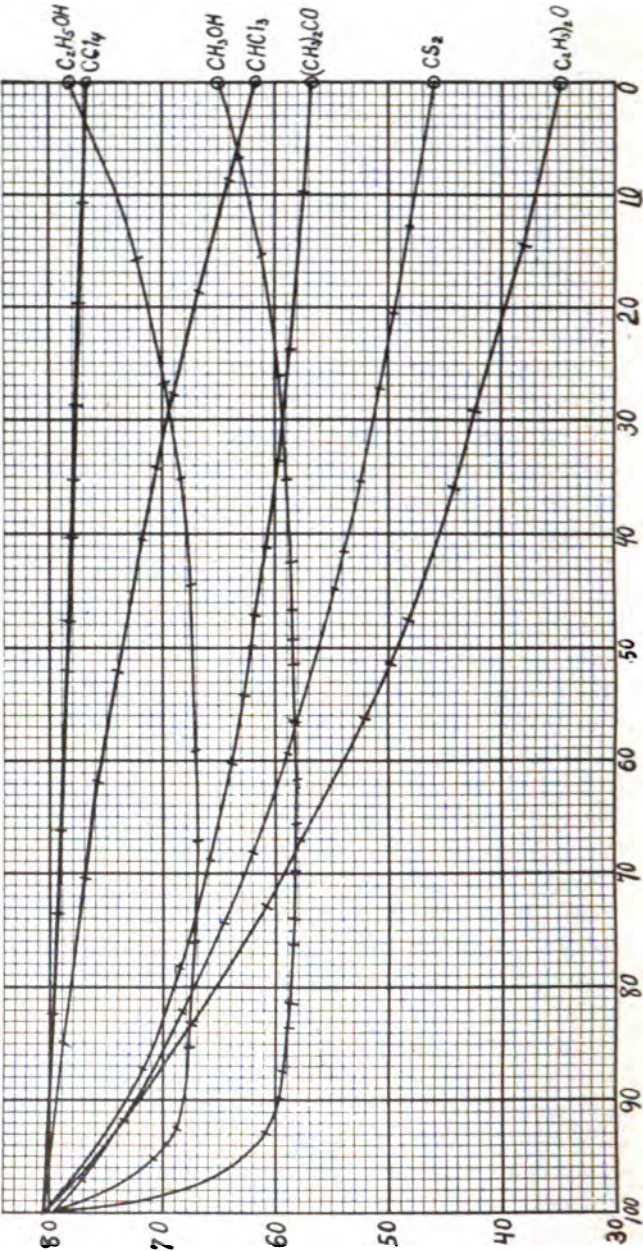
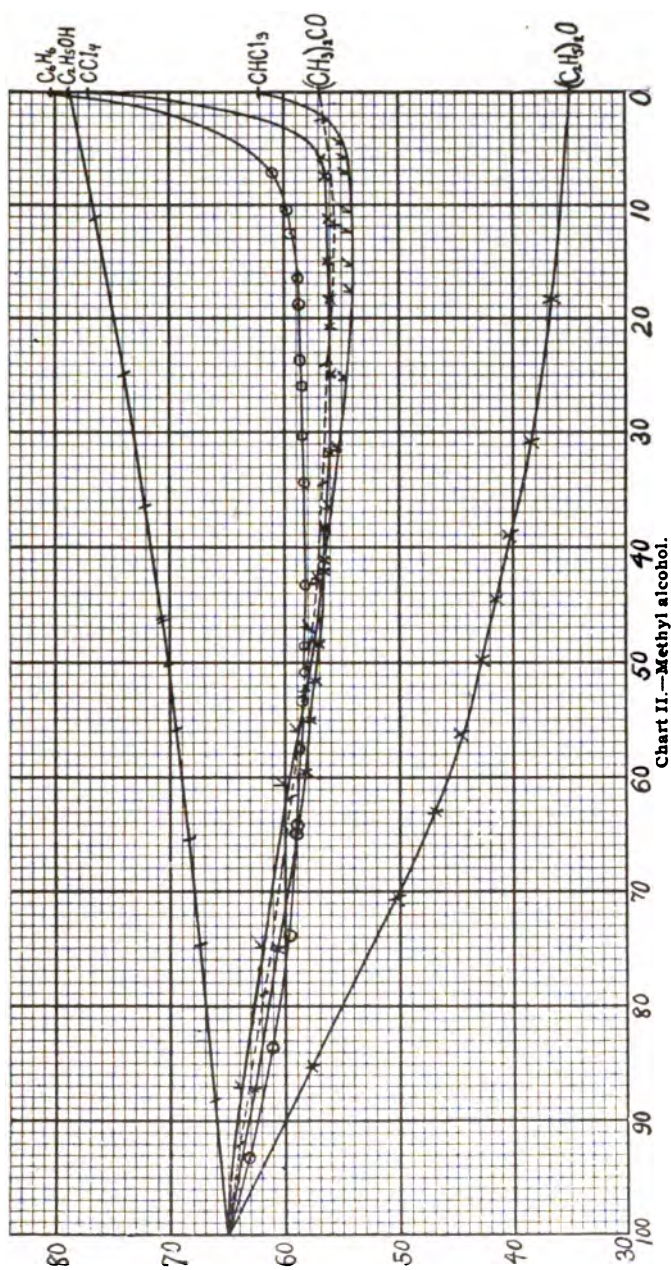


Chart I.—Benzene.



and carbon tetrachloride respectively both have minimum points, but need no further mention, as they have been fully discussed in my first paper.

If now the above chart representing the curves for methyl alcohol, is compared with the chart in paper I representing the curves for ethyl alcohol, it will at once be seen that the curves for the several liquids with methyl alcohol are quite similar to the curves for the same liquids with ethyl alcohol, each to each. Thus, the statement made in paper I, "In general, one constituent remaining the same, mixtures with substances of similar chemical constitution yield similar boiling-point curves," is borne out. The only exception one might pick out in these two sets of curves is when the methyl alcohol and acetone curve and the ethyl alcohol and acetone curve are compared. The first of these has a minimum point and the second has not. Granting, however, that this is the case, the minimum point of the methyl alcohol and acetone curve is only 0.8°C . below the boiling-point of the pure acetone, and the general shape of the curve is exactly the same as that of the ethyl alcohol and acetone curve.

From the data here presented the following conclusions may be drawn:

1. All mixtures of the following pairs of liquids boil at temperatures between the boiling-points of the constituents: Benzene and chloroform, benzene and carbon tetrachloride, benzene and ether, benzene and acetone, methyl alcohol, ethyl alcohol, and methyl alcohol and ether.

2. A solution containing 33 to 47 per cent. methyl alcohol in benzene distils without change at about 58.3°C . under a pressure of 760.7 mm. of mercury.

3. A solution containing about 18.4 per cent. methyl alcohol in carbon tetrachloride distils without change at 55.95°C . approximately under a pressure of 765.5 mm. of mercury.

4. The statement of paper I is borne out that "In general one constituent remaining the same, mixtures with substances of similar chemical constitution yield similar boiling-point curves."

5. Further, the statement in paper I is also borne out that: "The close proximity of the boiling-points of the constituents appears to be a favorable condition for the existence of a maximum or a minimum point on the boiling-point curve,

similarity of constituents seems to be a strongly modifying condition however.

Note.—Since sending the above article to press I am in receipt of a reprint of a paper entitled, "A Contribution to the Study of Liquid Mixtures of Constant Boiling-point," by Dr. Garnett Ryland,¹ in which are described his investigations of some of the same mixtures as are given in the above paper and paper I. They are benzene and chloroform, benzene and methyl alcohol, methyl alcohol and ether, methyl alcohol and acetone, and methyl alcohol and chloroform. His results are in the main the same as those obtained by myself, except in the case of methyl alcohol and acetone. He finds that this mixture can be separated by fractional distillation, while I find that the mixture has a minimum point about 0.8° C. below the boiling-point of the pure solvent.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 49.]

THE ELECTROLYSIS OF METALLIC PHOSPHATE SOLUTIONS.

BY HARRY M. FERNBERGER AND EDGAR F. SMITH.

Received August 2, 1899.

THE action of the current upon metallic phosphates, has received considerable attention in this laboratory. The frequent satisfactory repetition of these methods has only served to convince us that they deserve a permanent place in electrolytic literature, hence we take the present opportunity of again calling attention to them in their modified forms as to current density, voltage, etc., factors which were not especially emphasized in the earlier communications. Furthermore, other interesting behaviors of various metals in phosphate solutions, having come to light, we shall include them here. They are at least suggestive.

COPPER.

To a solution of copper sulphate, equivalent to 0.1239 gram of metal, were added twenty cc. of disodium hydrogen phosphate (sp. gr. 1.0358), and the precipitate produced was dissolved in five cc. of phosphoric acid (sp. gr. 1.347). The electrolytic

¹ Dissertation, Johns Hopkins University, 1898.

decomposition was then made with the following prevailing conditions:

N.D. ₁₀₀	0.035 to 0.068 ampere.
Voltage.....	2.2 to 2.6.
Dilution.....	225 cc.
Temperature.....	54°-64°.
Time	6 to 7 hours.

The deposit of copper weighed 0.1244 gram. It showed a deep red color. The metal could not be detected in the filtrate. A second trial gave 0.1243 gram of copper.

COPPER FROM IRON.

Sixty cc. of a disodium hydrogen phosphate solution (sp. gr. 1.0358) were added to twenty-five cc. of a copper sulphate solution (= 0.1239 gram of copper) and fifty cc. of a ferric ammonium sulphate solution (= 0.2002 gram of iron). The resulting precipitate was dissolved in ten cc. of phosphoric acid (sp. gr. 1.347). The conditions existing during the electrolysis were:

N.D. ₁₀₀	0.04 ampere.
Voltage	2.4.
Dilution.....	225 cc.
Temperature	53° C.
Time	7 hours.

The copper deposit weighed 0.1237 gram. Its color was brown-red, and it showed a silky luster. Iron was not found in it. The filtrate contained no copper.

COPPER FROM ALUMINUM.

To a solution containing 0.1239 gram of copper and 0.1000 gram of aluminum, were added sixty cc. of disodium hydrogen phosphate (sp. gr. 1.0338) and five cc. of phosphoric acid (sp. gr. 1.347). The conditions were:

N.D. ₁₀₀	0.068 ampere.
Voltage.....	2.6.
Dilution	225 cc.
Temperature.....	77°.
Time	6 hours.

The precipitated copper weighed 0.1240 gram. It was not contaminated with aluminum, nor did the filtrate show any signs of copper.

COPPER FROM CHROMIUM.

Sixty cc. of disodium hydrogen phosphate (sp. gr. 1.033) and 8 cc. of phosphoric acid (sp. gr. 1.347) were added to a solution containing 0.1239 gram of metallic copper and 0.1403 gram of chromium. The precipitation of metal then occurred with the following conditions :

N.D. ₁₀₀	0.062 ampere.
Voltage.....	2.5.
Dilution.....	225 cc.
Temperature.....	64°.
Time.....	6 hours.

The deposit of copper weighed 0.1243 gram. The filtrate did not show the presence of copper, nor could chromium be detected in the precipitated metal.

When the conditions given in the preceding separations are observed there need be no doubt as to the results.

COPPER FROM COBALT.

Sixty cc. of disodium hydrogen phosphate, and ten cc. of phosphoric acid were added to a liquid containing 0.1239 gram of metallic copper and 0.1000 gram of metallic cobalt. It was then electrolyzed with :

N.D. ₁₀₀	0.035 ampere.
Voltage.....	1.5.
Dilution.....	225 cc.
Temperature.....	62°.
Time.....	6 hours.

The precipitated copper weighed 0.1243 gram. It did not contain cobalt.

COPPER FROM ZINC.

Salts of these two metals, containing the same quantities of disodium hydrogen phosphate and phosphoric acid, were electrolyzed with:

N.D. ₁₀₀	0.035 ampere.
Voltage.....	2.5.
Dilution.....	225 cc.
Temperature.....	60°.
Time.....	5 hours.

The copper weighed 0.1244 gram, and was free from zinc.

COPPER FROM NICKEL.

A solution of copper sulphate (= 0.1239 gram of copper) and nickel nitrate (= 0.1366 gram of nickel) was mixed with seventy-five cc. of disodium hydrogen phosphate (sp. gr. 1.033) and ten cc. of phosphoric acid (sp. gr. 1.347). The conditions of electrolysis were :

N.D. ₁₀₀	0.072 ampere.
Voltage.....	2.45.
Dilution.....	225 cc.
Temperature.....	66° C.
Time.....	6 hours.

The precipitated copper weighed 0.1241 gram. The filtrate did not show the presence of this metal, and the deposit was free from nickel.

It was thought advisable to carry out the separation of copper in phosphate solution, not from a single metal alone, but from several, and note the most favorable conditions.

COPPER FROM IRON, COBALT, AND ZINC.

The solution contained 0.1239 gram of copper, 0.1007 gram of cobalt, 0.1000 gram of iron, thirty cc. of disodium hydrogen phosphate (sp. gr. 1.0358), and fifteen cc. of phosphoric acid (sp. gr. 1.347). The conditions of the electrolysis were :

N.D. ₁₀₀	0.04 to 0.05 ampere.
Voltage.....	2.3.
Dilution.....	225 cc.
Temperature.....	57°.
Time.....	6 hours.

The deposit of copper weighed 0.1240 gram. It was free from the other metals.

COPPER FROM MANGANESE.

A solution containing about equal amounts of the two metals together with sixty cc. of disodium hydrogen phosphate (sp. gr. 1.038) and ten cc. of phosphoric acid (sp. gr. 1.347), was electrolyzed with :

N.D. ₁₀₀	0.05 ampere.
Voltage.....	2.5.
Dilution.....	225 cc.
Temperature.....	56° C.
Time.....	6 hours.

The copper deposit weighed 0.1236 gram. The preceding determinations were all conducted with comparatively feeble currents.

Trials were made with stronger currents with several of the metals.

NICKEL.

Thirty cc. of disodium hydrogen phosphate were added to a nickel solution ($= 0.070$ gram of nickel), and the resulting precipitate was then dissolved in just sufficient phosphoric acid (1.347 sp. gr.) for that purpose, with several drops in excess. The electrolysis was then made with:

N.D. ₁₀₀	0.50 ampere.
Voltage.....	7-8.
Dilution.....	225 cc.
Temperature.....	68° C.
Time.....	3½ hours.

The precipitate of nickel weighed 0.0703 gram. The filtrate was found free from that metal. A second nickel solution ($= 0.1360$ gram of metal), forty-five cc. of disodium hydrogen phosphate (sp. gr. 1.038) and phosphoric acid (sp. gr. 1.347) sufficient to dissolve the precipitate, with a few drops in excess, was electrolyzed with:

N.D. ₁₀₀	0.53 ampere.
Voltage.....	7.
Dilution.....	225 cc.
Temperature.....	65°.
Time.....	3½ hours.

The nickel precipitate weighed 0.1360 gram. These deposits of nickel were dull gray in color, resembling the appearance to some extent of the platinum dish. They were very adherent, and were readily handled and washed. Notwithstanding the precipitation of the metal was complete, the attempts to separate it in this way from manganese and chromium were fruitless. On examining the deposit from the nickel and manganese solution it was found to contain phosphorus.

The use of stronger currents with zinc salts failed to give satisfactory results. A qualitative test made with cobalt seemed to indicate that this metal could be deposited with conditions similar to those used with nickel. A solution, containing both

iron and manganese, was also acted upon with a current similar to that employed with nickel and cobalt but neither of the metals was deposited. We were equally unsuccessful in depositing uranium from an acid phosphate solution.

MERCURY.

Twenty-five cc. of a mercuric chloride solution (= 0.1159 gram of metal), thirty cc. of disodium hydrogen phosphate (sp. gr. 1.038) and five cc. of phosphoric acid (sp. gr. 1.347), were electrolyzed with :

N.D. ₁₀₀	0.04 ampere.
Voltage.....	1.6.
Dilution	175 cc.
Temperature.....	50° C.
Time	4 hours.

The precipitated mercury weighed 0.1162 gram. It was silvery white in color and drop-like in appearance.

MERCURY FROM ZINC.

Twenty-five cc. of a mercuric chloride solution (= 0.1159 gram of metal), twenty-five cc. of zinc sulphate (= 0.1010 gram of zinc), sixty cc. of disodium hydrogen phosphate (sp. gr. = 1.038) and ten cc. of phosphoric acid (sp. gr. = 1.347), were electrolyzed with :

N.D. ₁₀₀	0.01 ampere.
Voltage.....	1.5.
Dilution	175 cc.
Temperature.....	60° C.
Time	4-5 hours.

The deposit of mercury weighed 0.1163 gram. It was free from zinc. The filtrate did not show any mercury.

The separation of mercury from cadmium did not succeed. As uranium was not precipitated under similar conditions we hoped for a separation of this metal from mercury and also from copper.

MERCURY FROM URANIUM.

A solution containing 0.1159 gram of mercury, 0.1018 gram of uranium, sixty cc. of disodium hydrogen phosphate (sp. gr. 1.038), and ten cc. of phosphoric acid (sp. gr. 1.347), was electrolyzed with :

N.D. ₁₀₀	0.017 amperes.
Voltage.....	2.45.
Dilution.....	175 cc.
Temperature.....	61° C.
Time	5½ hours.

The deposit weighed 0.2370 gram. It was heavier, therefore, than the combined weights of the mercury and uranium. A second trial was made after increasing the volume of phosphoric acid to fifteen cc. The deposit weighed 0.2012 gram. It had a dull lead color. It was strongly ignited to expel the mercury. The scaly residue was boiled with dilute nitric acid and the solution tested with ammonium molybdate. Large amounts of phosphorus were indicated. This would prove that the original deposits of metallic mercury so influenced the uranium salts that they were coprecipitated with that metal. Whatever the composition of the deposit may be it is certainly very variable. It is quite probable that a hydrous uranium phosphate is deposited with the mercury. The filtrates were all free from uranium.

On trying to effect the separation of copper from uranium in acid phosphate solution we experienced the same difficulty as with mercury and uranium. The precipitate consisted of copper, uranium, and phosphorus. The filtrate showed no signs of either copper or uranium. The separation of mercury and manganese was far from satisfactory. The same must be said of nickel and cobalt. They were partially precipitated with the mercury and carried down phosphorus with them. A qualitative test was made to separate uranium in the presence of mercury and phosphoric acid, electrolytically from iron. The deposit contained no iron when a current of $N.D._{100} = 0.006$ ampere was employed. This separation will receive further study in the immediate future.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
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OBSERVATIONS UPON TUNGSTEN.

By EDGAR F. SMITH.

Received August 5, 1899.

THIS communication presents fragmentary data upon tungsten collected during a period of years and amply verified by repeated reviews. As tungsten in its various combinations has been an object of great interest to the writer, particularly

the question as to its atomic mass, it need not surprise the reader to find that recourse has been had to so many diverse derivatives in the search for some body which would possess a constitution and properties suitable for an investigation of the problem. In the course of the study numerous observations were made which are not wholly devoid of interest and which are now incorporated in the following paragraphs. The solubility of tungsten trioxide and its derivatives in sulphur chloride deserves consideration; as do the facts that the third oxygen atom defies removal in this way and that pure sulphur chloride does not attack metallic tungsten, hereby enabling us to eliminate the final traces of oxides. The great volatility of the trioxide, on exposure to heat, condemns the ignition of metal in air as a means of deriving the atomic mass. Then, too, the establishment of a crystalline oxide is of some moment. Why the alkyl derivatives failed to appear is difficult to understand. If they could be prepared they would, doubtless, afford a splendid means of determining the atomic mass. Perhaps in the near future we shall find some method of making them. However, it is possible that the more metallic nature of tungsten will prohibit the formation of stable alkyls as seems obvious with the esters of tungstic acid.

For the experimental part of the work the writer is indebted to the several gentlemen whose names are given in the proper places and would here return them his sincere thanks for their kind and indispensable assistance.

I. THE ACTION OF SULPHUR MONOCHLORIDE UPON TUNGSTEN TRIOXIDE.

BY HERMANN FLECK.

Attention has been directed to the action of sulphur monochloride upon various natural sulphides and oxides.¹ The purpose, primarily, of my study was to ascertain the nature of the body produced when tungsten trioxide, or any of its naturally occurring combinations, *e. g.*, wolframite or scheelite, were heated together with sulphur monochloride to 145° C. On cooling scarlet-red, prismatic needles, one of which measured two and one-half inches, crystallized from the red solution. On exposure to the air they immediately decomposed, evolving hydrochloric

¹ This Journal, 20, 289.

acid, and changing to tungsten trioxide. They dissolved freely in carbon disulphide and sulphur monochloride, but sparingly in benzene. The first crops were impure and gave very unsatisfactory analytical results. To eliminate a yellow powdery substance, admixed with the crystals, the following course was pursued: a tube containing the scarlet crystals, yellow powder, and mother-liquor from which the pressure had been released, was resealed and placed in an upright position in a tall beaker containing boiling water. The sulphur chloride became blood-red in color due to the dissolved crystals. The tube was now carefully inclined and the liquid drained away from the heavy yellow substance into the other end of the tube. The solution cooled instantly and a nest of beautiful crystals separated from it. This procedure was repeated until a complete separation of the two bodies had been achieved. Having finally removed the scarlet crystals from the tube they were further purified by sublimation and recrystallization from suitable solvents. With proper care and exclusion of moisture both courses yielded satisfactory results.

- In the sublimation process five to ten grams of the crystals were placed in a wider tube with a three-holed stopper, carrying an inlet and exit tube as usual and a thermometer. The apparatus was filled with perfectly dry carbon dioxide and heat applied. First a ring of condensed mother-liquor made its appearance. The red crystals became dark in color and began to boil at 215° . The volatilization was complete at 225° . By careful fractional sublimation into bulbs filled with carbon dioxide magnificent scarlet crystals were obtained. These were analyzed. They showed the presence of 53.53 per cent., 53.59 per cent. and 53.94 per cent. of tungsten with 40.99 per cent. of chlorine; no sulphur was found. The oxychloride of tungsten (WOCl_2) required 53.94 per cent. of tungsten and 41.38 per cent. of chlorine.

The product of the interaction of sulphur monochloride and tungsten trioxide is, therefore, tungsten oxytetrachloride— WOCl_4 . Again, a large mass of crystals after removal from the tube was quickly pressed between paper and recrystallized from small quantities of sulphur chloride with which it was boiled and subsequently allowed to cool in an Erlenmeyer flask. After

being freed in this way from the mother-liquor containing sulphur, they were washed with carbon disulphide previously dehydrated by standing over sodium wire. The adhering carbon disulphide was expelled in a current of dry carbon dioxide and the flask was then tightly stoppered. The flask and contents were weighed and a portion of the material removed, after which the flask was reweighed. The quantity of substance for analysis was thus found by difference. The analysis showed the presence of 35.51 per cent. of tungsten and 39.5 per cent. of chlorine. When it is considered that over seven grams of material were used in the estimation of the tungsten, eleven grams for the chlorine and even a larger quantity for the sulphur, the results will not fail to win favor. That the chlorine content is low is not astonishing if we recall how tenaciously moist tungsten trioxide retains hydrochloric and sulphuric acids.

These analytical results and the boiling-point of the scarlet crystals, establish their identity as tungsten oxychloride.

Tungsten dioxide was also changed to the same body on heating it with sulphur monochloride. Even when the oxides were exposed with the sulphur chloride to temperatures as high as 240° , the third oxygen atom was not displaced. Tungsten hexachloride and tungsten dioxychloride were never observed.

The action of sulphur chloride upon tungsten metal was also tried. The result of this study showed that pure sulphur chloride, free from chlorine, has no action upon the metal, but when that gas is present in sufficient quantity the metal can be completely changed to the hexachloride, crystallizing in steel-blue needles and forming dark red vapors. With an insufficiency of chlorine, black crystals are produced. These were found to be hexachloride contaminated with metallic tungsten.

Finely divided wolframite and scheelite, as already noted, are also soluble in sulphur monochloride. It may be added that this method affords an excellent means of preparing the red oxychloride. Indeed, it seems to be a superior method in every way for that purpose.

I shall now return to an observation noted in the first section of this communication; *viz.*, that tungsten trioxide used in atomic mass work did not entirely dissolve in sulphur chloride when heated to 145° C. Further, it was always necessary to free the

oxychloride from adherent trioxide. Why, if this be pure oxide of tungsten, does it not dissolve completely? Can it be that this insoluble part is the impurity in the oxide which affects the atomic mass? Is it perhaps a nitride, or oxynitride, or some allotropic modification of the trioxide? These questions suggested themselves from time to time and efforts were made to answer them. How this was done will appear in the following paragraphs:

1. Two grams of tungsten trioxide, made from ammonium tungstate, were heated to 145° with sulphur monochloride. On cooling the red crystals separated from the solution, leaving, however, much unattacked original material. The crystals were roughly separated from the deposit, pressed between folds of filter-paper, and then allowed to decompose in the air. They were moistened, ignited to the trioxide and reheated in a sealed tube with sulphur monochloride. This trioxide disappeared almost entirely at 140° – 170° , yielding the red crystals as before. The portion remaining unattacked was washed with carbon disulphide, dried, and ignited. It weighed six-tenths gram. When reheated with sulphur monochloride at 140° – 170° it did not dissolve. Larger quantities of ignited tungsten trioxide were treated in this way and thus separated into two distinct parts, each of which was exposed to the action of sulphur chloride until it ceased to dissolve any more. From 150° – 180° there was no further action on the insoluble portion. This point is also indicated by the sulphur chloride no longer assuming a red color due to the oxychloride which it may contain. The oxide from the red crystals, when decomposed and ignited, left a portion of substance insoluble in sulphur monochloride. Could it be that in the ignition of this oxide there was something abstracted from the air that rendered it insoluble in sulphur monochloride? If this were true then it could be readily understood why the oxide prepared by the ignition of ammonium tungstate was so largely insoluble in the sulphur chloride. It would also account for some of the discrepancies noticed in the atomic mass determinations.

2. To demonstrate that the trioxide changes either to an allotropic modification or to some other body, by ignition in air, a sample of it was made by heating moistened oxychloride as gen-

tly as possible. It was then divided into two equal portions (*a* and *b*) of one gram each in weight.

a was placed directly into a tube with S_2Cl_2 and heated for eight hours from 150° – 170° .

b was *not* placed directly into a tube but was heated alone for eight hours in air at a high temperature and then exposed for eight hours to the action of sulphur chloride at 150° – 170° .

The contents of *a* were completely dissolved, whereas those of *b* were unattacked. The question remained—what is this insoluble substance?

3. All the material which had previously proved insoluble in sulphur chloride was now collected and heated with this reagent in sealed tubes to 250° . *Its solution was complete.*

4. Possibly the insoluble compound represented an oxynitride. I thought this might be ascertained by analyzing the air in which the trioxide was ignited or by proving the presence of nitrogen in the insoluble material.

5. To demonstrate the falsity or correctness of the idea of an oxynitride having been produced, a portion of tungsten trioxide, soluble in sulphur chloride, was placed in a porcelain tube between two asbestos plugs. At one side was attached a reservoir, consisting of a wide tube, connected by rubber tubing to a second tube of about the same capacity. A regular Hempel burette and leveling tube were joined to the opposite end of the porcelain tube. Mercury was filled into the tubes and a definite volume of air into the burette, the oxygen of which had been accurately determined in another portion of it. Heat was applied to the tube and the air was passed back and forth over the trioxide by raising and lowering the leveling tubes alternately on both sides of the combustion tube. The heating process continued for three hours. After cooling the volume of air had not diminished. Neither nitrogen nor oxygen had been absorbed. *The oxide was not soluble in sulphur chloride.*

6. A portion of the "insoluble" material was placed in a hard glass tube and heated in an air current, which then passed into water, but no reaction for either nitric or nitrous acid was observed.

7. A tube of hard glass, sealed at one end and containing stick caustic potash, was attached to a vacuum pump and heated.

When it had melted and the gas particles enclosed in it had escaped, the tube was cooled and after the introduction of from ten to fifteen grams of the "insoluble" trioxide it was carefully exhausted and sealed. Its contents were heated, when the "insoluble" oxide dissolved. Any nitrogen that might have been present would have been expelled as such or in the form of ammonia. On opening the tube under mercury the latter filled it completely. Gases were not present.

II. TUNGSTEN ALKYL.

BY E. A. BARNETT.

Riche¹ claims that when he heated metallic tungsten with methyl iodide to 240° in a sealed tube for ten days he obtained a product that upon distillation yielded unaltered methyl iodide and a viscous liquid. The latter only distilled at high temperatures. When it was shaken with a little warm ether-alcohol an oily substance separated, while the ethereal solution contained a compound melting at 110° and crystallizing in colorless plates. To this body he ascribed the formula $W(CH_3)_4I$. Cahours,² believing that the saturation power of W was WX_4 , repeated the work and obtained the same body. I endeavored to prepare it with the purpose of making other alkyl derivatives in order to use the same in the redetermination of the atomic mass of tungsten. I heated one part of tungsten with four parts of methyl iodide for ten days to 240°. On opening the tubes a sharp, acid, unpleasant odor was noticed. The contents of the tubes were distilled out in a steam-bath. The distillate boiling at 42° proved to be methyl iodide. What remained in the tube was treated with ether-alcohol and filtered. The ether-alcohol solution was allowed to evaporate spontaneously; a greenish black mass remained but colorless crystals were not discernible. The residue was extracted with chloroform and this solution placed aside to crystallize. After standing awhile, plate-like forms appeared. These disclosed the presence of iodine upon applying the test. They also contained tungsten. Thus, 0.2765 gram of material yielded 0.2604 or 93.45 per cent. of tungsten. Two other determinations made with more care gave 94.38 per cent. and 94.31 per cent. of tungsten, respectively. Concentrated nitric acid,

¹ *Jsb. d. Chem.*, p. 373 (1856); *Compt. rend.*, 42, 203 (1856); *J. prakt. Chem.*, 69, 10.

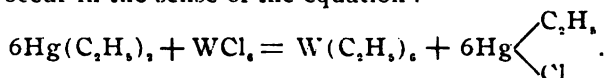
² *Ann. Chem. (Liebig)*, 122, 70.

acting on the compound, liberated iodine vapors. The same was observed when heat was applied to the compound. Two determinations of the iodine content were made showing the presence of 1.18 per cent. and 1.58 per cent., respectively.

To ascertain whether the compound contained carbon, portions of it were carefully burnt in an air current, the gases being conducted into lime-water. A precipitate of calcium carbonate was produced. It was filtered out, and from its lime content the corresponding percentage of carbon was calculated. In this way were found 1.99 per cent. and 2.01 per cent. of carbon, respectively.

These results do not indicate a tungsten alkyl, but rather finely divided metal with carbon and adherent methyl iodide.

Tungsten hexachloride and mercury ethide were allowed to interact in ligroin solution. A dark blue mass resulted; this on standing became purplish black in color. I hoped that a change might occur in the sense of the equation :



The reaction product was transferred to a filter and washed with cold ligroin, after which it was introduced into a Soxhlet apparatus and extracted with benzene for three hours. Its color was dark blue or purple. This was dried over sulphuric acid and analyzed :

	Tungsten. Per cent.	Chlorine. Per cent.
Found (in a)	46.33	9.55
" (in b)	46.27	9.21

Carbon was not present. Analyses of other portions revealed the presence of varying amounts of mercury and chlorine.

It is safe to conclude that an alkyl derivative of tungsten cannot be produced in this way. Indeed, I cannot help but doubt the existence of these bodies, for my experiments are not all which have been tried in this laboratory and which have resulted negatively. As little success has been had with molybdenum along similar lines.

III. TUNGSTEN ALKYLs.

By CLARENCE HALL.

It was my aim to prepare the alkyls of tungsten by the use of

zinc methide and a tungsten chloride. To this end I placed a bulb, containing three and seven-tenths grams of zinc methide, and another containing three and two-tenths grams of tungsten hexachloride in a glass tube sealed at the one end, while its other end was drawn out and through this contracted tube was passed a much smaller tube conveying dry nitrogen. This gas was allowed to pass for more than half an hour through the tube, after which the latter was sealed. By shaking it, the bulbs containing the zinc methide and tungsten hexachloride were broken. When their contents came together heat and light were produced and a black substance separated. After this the tube was heated for a period of six hours at a temperature of 70° . A decided pressure was noticed when the tube was opened. The tube contents were treated with ether and the solution examined for tungsten compounds. They were not found present. The residue showed the presence, on analysis, of tungsten, zinc, carbon, and hydrogen. The ratio of these constituents was indefinite. A second trial resulted similarly, so that I gave up all hope of preparing the alkyl body in this manner.

Thinking that possibly in the direct action of the alkylogens upon tungsten metal the character of the latter influenced the reaction, I concluded to act:

1. With methyl iodide upon tungsten obtained by passing sodium vapors in an atmosphere of hydrogen over gently ignited tungsten trioxide. The tube contents after exposure to 200° for from eight to ten days were treated and examined as indicated by Riche. The residue, on analysis, showed 1.71 per cent. of carbon, 91.33 per cent. of tungsten, 1.5 per cent. of iodine, and 0.34 per cent. of hydrogen.

2. The metal in this series of experiments was prepared by fusing tungsten hexachloride with metallic sodium. The resulting product was extracted with water and the tungsten was then further purified by alcohol and carefully dried. It was heated as before with methyl iodide. In this instance the alcohol-ether layer on evaporation left a white scaly substance which melted at 115° . It revealed the presence, on testing, of iodine, tungsten, and carbon. Had I really found Riche's compound? This I firmly believed until other experiments made in this lab-

oratory proved that this substance was nothing more than sodium iodide mixed with some ethereal tungsten body.

IV. ESTERS OF TUNGSTIC ACID.

BY CLAUDE DUGAN.

Several chemists have recorded their experiences in preparing these compounds. Göessmann¹ endeavored to form them by allowing alkyl iodides to act upon silver tungstate, but was unsuccessful. Subsequently, Maly² obtained through the action of ethyl alcohol upon tungsten oxychloride ($WOCl_4$) a white flocculent precipitate, which after washing with alcohol was allowed to dry in the air and later over sulphuric acid, when it became a hard, brittle vitreous mass. A single analysis of it gave 85.16 per cent. of tungsten, 5 per cent. of carbon, and 1.64 per cent. of hydrogen, pointing, in the judgment of Maly, to an ester of metatungstic acid, $W_2O_5.H.C_2H_5 + H_2O$.

I repeated this experiment, obtaining a body which revealed the presence of 79.6 per cent. of tungsten, 1.06 per cent. of carbon, and 0.84 per cent. of hydrogen.

Not doubting in the least the observation of Maly, but thinking probably that the reaction or transposition was not as simple as might be inferred upon reading his paper and that by the action of the hydrochloric acid, evolved in the change, upon the unconsumed alcohol present, water would be produced and this in turn would form varying amounts of tungstic acid which naturally would contaminate the resulting ester, I studied the action of other alcohols in a pure and dry state upon beautifully crystallized and purified tungsten oxychloride.

First, let me present my experience with isobutyl alcohol in the line indicated. When it and the oxychloride were brought together much heat was evolved; a yellow precipitate separated after standing. The filtrate from this was distilled under reduced pressure, when a white starchy mass appeared. This was dried over phosphorus pentoxide and soda-lime. When nearly dry it was dissolved in anhydrous ether. To the ethereal solution pure anhydrous ethyl alcohol was added with the production of a gelatinous white precipitate which was collected and carefully handled until dry and ready for analysis. It was

¹ *Ann. Chem. (Liebig)*, 101, 218.

² *Ibid.*, 139, 240.

a very brittle powder and contained 7.4 per cent. of carbon, 1.60 per cent. of hydrogen, 65.00 per cent. of tungsten, and 5.76 per cent. of chlorine, which closely approximate the requirements of a compound of the formula



In other words the transposition between the oxychloride and the alcohol was not complete and to the new product there was added hydrated tungstic acid. Whether it is possible to effect a complete transformation and whether the ester can be isolated without contamination with tungstic acid, appears to me rather doubtful. I am led to this view because upon substituting other alcohols and proceeding in the manner of Maly, I invariably obtained products of complex character, containing tungsten, carbon, hydrogen and chlorine. Thus with propyl alcohol a product was isolated which showed the presence of 10.3 per cent. of carbon, 4 per cent. of hydrogen, 6.3 per cent. of tungsten and 5.32 per cent. of chlorine. With amyl alcohol the case was practically the same, and it seems evident that while esters of tungstic acid do perhaps exist they can only be isolated with extreme care and are surrounded by conditions which favor their ready and rapid breaking down. It must be admitted, however, that the tungstic acid in yielding these incomplete esters exhibits the character peculiar to the group in which it is placed by the periodic system and the instability of the desired and expected derivatives must be attributed to the absence of a sufficiently pronounced acid, or non-metallic, nature in the tungsten itself.

V. THE ATOMIC MASS OF TUNGSTEN.

BY WILLETT L. HARDIN.

In an article published from this laboratory last year¹ it was demonstrated that the method usually employed in the determination of the atomic mass of tungsten is unsatisfactory. The results given in that paper were obtained by the reduction of tungsten trioxide in a current of hydrogen at a white heat, and the subsequent oxidation of the metal in air. Like the determinations of earlier experimenters, these results showed considerable variation; the maximum and minimum values for the atomic

¹ This Journal, 19, 657.

mass of tungsten differed as much as one and a half units. Some of the probable causes of these deviations were also discussed and certain sources of error pointed out.

It was proved, for example, that tungsten trioxide obtained from ammonium tungstate contains nitrogen; that the oxide of tungsten is slightly volatile or that a small portion is carried out mechanically by the water formed in the reduction; and also, that tungsten attacks the vessels in which the atomic mass determinations have been made.

The following experiments were undertaken in the hope of gathering further evidence as to the cause of these variations, and with a view of arriving at a more satisfactory conclusion in regard to the true atomic mass of tungsten.

Tungsten trioxide resulting from experiments made last year was heated to 145° in sulphur monochloride in a sealed tube. About 75 per cent. of the oxide was taken up by the sulphur chloride. When the solution cooled, red crystals separated; these were removed from the unattacked material and after washing with carbon bisulphide were ignited in a current of oxygen, and the oxide thus prepared was reduced in hydrogen.

	Tungsten trioxide. Grams.	Tungsten. Grams.	Atomic mass of tungsten.
1.....	2.42690	1.90610	175.68
2.....	1.62225	1.28195	180.80

The metal from these reductions was reoxidized:

Tungsten. Grams.	Tungsten trioxide. Grams.	Atomic mass of tungsten.
1.24369	1.56691	184.69

On reducing this oxide, the value 183.75 was obtained for the atomic mass of tungsten.

From these experiments it is obvious that the material produced by the ignition of the red crystals is not pure tungsten trioxide. A portion of it was reduced in hydrogen and the volatile products conducted through a solution of copper sulphate. A black precipitate of copper sulphide was thrown down, showing that the substance retained sulphur, even after it had been ignited in a current of oxygen.

When the metal from the red crystals was oxidized and the

product heated in sulphur monochloride in a sealed tube at a temperature of 145° , only a portion of it was taken up. This insoluble portion was supposed, at first, to contain nitrogen. A series of observations were made to decide this point.

The first experiment consisted in oxidizing the metal obtained from the red crystals in an atmosphere of commercial oxygen. This was carried out in an asbestos cell, the interior of which was covered with plaster of Paris. The crucible containing the metal was placed in an opening in the bottom of the cell, and a current of oxygen was introduced through a small glass tube which passed through the cover. This arrangement was used for a number of experiments but was unsatisfactory owing to the rapidity with which metallic tungsten oxidizes in an atmosphere of oxygen. The gas was taken up more rapidly than it could be supplied and consequently air passed into the cell around the sides of the crucible. In a second device the metal was oxidized in a combustion tube, the outlet of which was a long narrow tube, immersed at the lower end in mercury or sulphuric acid. This contrivance was very satisfactory in oxidizing the metal away from air.

The oxide obtained in this manner was more insoluble in sulphur monochloride than that obtained by the ignition of the metal in air.

The oxygen employed in these experiments, was then analyzed and found to contain six per cent. of nitrogen. An attempt was, therefore, made to obtain pure oxygen from potassium chlorate and manganese dioxide and from potassium chlorate alone. The gas was collected over recently-boiled distilled water. In every case the oxygen was found to contain about one per cent. of impurity, supposed to be nitrogen, but when tested was discovered to be carbon monoxide. The main object, however, was to get oxygen free from nitrogen; this was accomplished. Metallic tungsten was then oxidized in it, as already described, and the resulting oxide was found to be insoluble in sulphur monochloride at 145° .

The soluble and insoluble portions of oxide were next tested for nitrogen by reducing in hydrogen and conducting the resulting vapors into a dilute, standardized solution of hydrochloric acid. The strength of the acid was not perceptibly changed,

showing that not more than a trace of ammonia could have been formed.

The two portions of oxide were further tested for nitrogen by fusing with potassium hydroxide in a sealed glass tube which had been previously exhausted by means of a Geissler pump. The potassium hydroxide was fused before use and allowed to cool in a vacuum. After fusing the oxide with caustic potash, the contracted end of the tube was immersed in mercury and the tip broken off. The mercury completely filled the tube, showing that no gases had been set free in the reaction.

Atomic mass determinations were then made, using first the insoluble and afterward the soluble oxide. The trioxide, resulting from the ignition of the metal in air, was treated with sulphur monochloride at 145° . The insoluble portion was removed from the tube and reduced in a current of hydrogen. The resulting metal was oxidized in a current of oxygen and the following result obtained :

Tungsten. Grams.	Tungsten trioxide. Grams.	Atomic mass of tungsten.
2.68250	3.38144	184.20

The red crystals were then removed from the tube, heated in a current of oxygen and reduced in hydrogen. The resulting metal was oxidized as before :

Tungsten. Grams.	Tungsten trioxide. Grams.	Atomic mass of tungsten.
1.90428	2.40021	184.27

The two results are almost identical.

There appears then to be no difference in the composition of the soluble and insoluble oxides. The identity in their composition is also confirmed by the fact that one form can be converted into the other and *vice versa*. If the insoluble portion is converted into ammonium tungstate, the oxide resulting from the ignition of this salt is soluble in sulphur monochloride at 145° . When the metal obtained from the red crystals is oxidized in a current of oxygen, the resulting oxide is insoluble in sulphur chloride at 145° .

From these observations it seems that tungsten trioxide exists in two forms. To decide this point portions of the oxide were obtained by different methods, and carefully examined. One

portion of the material resulted from the oxidation of metallic tungsten in pure oxygen under a slightly increased pressure. An extremely high temperature was obtained by this procedure. Most of the oxide fused together in an opaque crystalline mass in the bottom of the boat, while a portion of it sublimed in beautiful, shining crystals on the sides of the boat. The fused mass seemed to be striated, indicating a prismatic structure. The sublimed crystals, however, appeared to be of a tetrahedral form. By strongly heating metallic tungsten in the air, Bernoulli¹ and Schafarik² obtained microscopic crystals of tungsten trioxide. By fusing the oxide with borax Nordenskjöld³ also obtained small crystals. This is sufficient evidence to show that tungsten trioxide exists in two forms, the amorphous and crystalline. The latter form is produced from the former at high temperatures.

A sample of the oxide was then prepared by the ignition of ammonium tungstate in air, and another portion by the ignition of metallic tungsten in air. A series of specific gravity determinations were made, using these various samples of oxide. The results were as follows :

SPECIFIC GRAVITY OF TUNGSTEN TRIOXIDE.

Fused mass	7.502
Sublimed crystals	7.301
From ignition of tungsten in air	7.272
From ammonium tungstate.....	5.804
“ “ “	5.705
“ “ “ (after high heating)	6.391
“ “ “ (“ “ “)	6.820

These results leave no doubt as to the existence of two forms of tungsten trioxide. The specific gravity determinations of earlier experimenters point to the same conclusion :

Heraopath.....	5.274
d' Elhujar	6.120
Karsten	7.130
Nordenskjöld	6.30-6.38
Zettnow.....	7.16-7.23

¹ Pogg. Ann., 111, 595.

² Sitzungsber. d. Akad. d. Wissenschaften in Wien.

³ Pogg. Ann., 114, 246.

The determinations of Nordenskjöld were made with crystals obtained by fusing tungsten trioxide with borax. Under suitable conditions then, it seems that the yellow oxide of tungsten polymerizes.

DETERMINATION OF THE ATOMIC MASS OF TUNGSTEN BY THE
OXIDATION OF THE METAL IN PURE OXYGEN.

After obtaining oxygen free from nitrogen, it was thought advisable to make use of this gas instead of air, in determining the atomic mass of tungsten by the oxidation method. The metallic tungsten was oxidized in a porcelain boat in a combustion tube. It was noticed in each experiment that a white sublimate was formed in the glass tube. The values obtained varied from 184.1 to 184.8. These results are of little value owing to the volatilization of the material.

An attempt was made to eliminate the error due to the volatilization of the oxide, by placing the boat containing the material in a glass tube, about twenty cm. in length, which had been drawn out to a small opening at one end. This tube together with the boat and contents was carefully weighed and placed in a larger combustion tube in which the oxidation was carried out. A sublimate was formed inside the smaller tube, and also on the walls of the combustion tube near the ends of the weighed tube. The results from these experiments are of no more value than those obtained without the use of the second tube.

A series of observations was next made to determine the amount of volatilization in the oxidation of a definite quantity of metallic tungsten. The same material was oxidized and reduced a number of times without being removed from the porcelain boat. The amount of volatilized oxide was not constant. The following results were obtained :

	Grams.
Weight of WO_3 at the beginning of the experiment..	2.36815
" " " after one reduction and reoxidation..	2.36780
" " " " two reductions and reoxidations	2.36560
" " " " three " " "	2.36430
" " " " four " " "	2.36401

Pure oxygen was used in these experiments. A sublimate was formed, however, when the metal was oxidized in air.

From these trials it is evident that no reliable atomic mass

determinations can be made by the oxidation of metallic tungsten either in air or in pure oxygen. The volatilization of substance would increase the values obtained for the atomic mass. No doubt this will explain why the results obtained by the oxidation method are, in general, higher than those obtained by the reduction method.¹

OCCCLUSION OF HYDROGEN BY METALLIC TUNGSTEN.

The occlusion of hydrogen by metallic tungsten has been suggested by some chemists as a probable source of error in the determination of the atomic mass of this element by the reduction and oxidation methods. Waddell² claims that no such occlusion occurs. Derenbach,³ on the other hand, says that an appreciable quantity of hydrogen is retained by the finely divided metal. In the observations on the atomic mass of tungsten which were published from this laboratory last year, attention was called to the fact that the results obtained were the same whether the metal was cooled in an atmosphere of hydrogen or in a vacuum. In order to definitely settle this question the following experiments were made:

Metallic tungsten which had been allowed to cool in an atmosphere of hydrogen was oxidized in a current of carefully dried oxygen. The vapors resulting from the oxidation were conducted through a U-tube filled with glass wool and phosphorus pentoxide. The results of three experiments are as follows:

	Tungsten. Grams.	Water obtained. Gram.
1	2.5	0.00005
2 ..	2.8	0.00070
3	3.0	0.00070

The quantity of hydrogen converted into water in these experiments is inappreciable in quantitative determinations.

In a second series of observations metallic tungsten was oxidized in a current of oxygen and the volatile products were collected over mercury, where they were carefully tested for hydrogen. The results were wholly negative. This precaution was taken owing to the fact that only a minute quantity of hydrogen was converted into water during the oxidation.

¹ See Pennington and Smith: *Ztschr. anorg. Chem.*, (1895).

² *Am. Chem. J.*, 8, 280 (1886).

³ Thesis, Würzburg (1892).

From these and earlier experiments it is evident that no appreciable error in atomic mass determinations is introduced by the occlusion of hydrogen by the metallic tungsten.

EXPERIMENTS ON TUNGSTEN OXYCHLORIDE ($WOCl_2$).

The red crystals, resulting upon heating tungsten trioxide with sulphur monochloride in a sealed tube, were found to be the oxychloride. An attempt was made to determine the atomic mass of tungsten from analyses of this compound. The substance was removed from the sealed tube into a larger combustion tube, filled with carbon dioxide. It was then sublimed, in a current of carbon dioxide, into small glass bulbs which were afterward sealed off. The analysis was carried out in the following manner :

One of the bulbs containing a portion of the sublimed material was carefully weighed. The tip was then broken off and the bulb quickly introduced into a glass-stoppered distilling flask containing strong nitric acid. When the acid was heated the chlorine content of the crystals was changed to oxychlorides of nitrogen and free chlorine. These gases were expelled from the flask and collected over an aqueous solution of silver nitrate, previously saturated with silver chloride. The solution was contained in a long-necked, inverted flask. The vapors were allowed to remain in contact with the liquid until the chlorine was completely changed to silver chloride. The quantity of silver chloride formed was determined in the usual manner, using a Gooch crucible. All the washings were made with water containing a little nitric acid and saturated with silver chloride. The tungstic acid, which remained in the flask, was ignited and weighed as the trioxide.

A large series of analyses were made but the results were too discordant to establish anything with certainty. Upon careful examination it was discovered that the red crystals, even after sublimation, contained varying quantities of sulphur as an impurity. It was also found that the tungstic acid in the distilling flask retained chlorine. Traces of the latter could be detected in the oxide after ignition. In view of these difficulties the method was given up as valueless for atomic mass determinations.

PRECIPITATION OF SILVER BY MEANS OF METALLIC TUNGSTEN.

Smith¹ showed that silver could be precipitated as metal from an ammoniacal solution of the nitrate by means of metallic tungsten. The results proved that six atoms of silver were precipitated for each atom of tungsten added. Thinking that this method might prove of value in determining the atomic mass of tungsten quite a number of observations were made.

The silver used in the experiments was purified by the Stas method. The nitrate obtained from this metal was dissolved in pure water in a platinum dish; a slight excess of ammonium hydroxide was then added to the solution. Finely divided metallic tungsten was next added in sufficient quantity to precipitate about one-half of the silver present. The solution was digested for some time in the cold, and the quantity of silver, which had been precipitated, was then determined. Many of the results for the atomic mass of tungsten were close to the theoretical while others showed considerable variation. The quantity of ammonia in the solution was varied and experiments were made at different temperatures but the results were too variable to establish anything with certainty. The precipitated metallic silver was then carefully examined and found to contain small quantities of silver tungstate. Notwithstanding the presence of this substance, the results in many instances were close to the theoretical. The method, however, will not answer for atomic mass determinations.

EXPERIMENTS ON BARIUM METATUNGSTATE.

By estimating the water of crystallization in barium metatungstate, Scheibler² endeavored to determine the atomic mass of tungsten. His results varied more than one unit. The values from the determinations of barium and tungsten were rejected by him. In reviewing the work on tungsten, it was thought advisable to repeat these experiments.

The material was prepared in a manner similar to that described by Scheibler; sodium metatungstate was formed by boiling a solution of the normal salt with tungstic acid. The salt, which was obtained with difficulty by this method, was recryst-

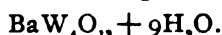
¹*Ztschr. anorg. Chem.*, 1, 360 (1892).

²*J. prakt. Chem.*, 83, 324 (1861).

tallized. Pure barium chloride was prepared by recrystallizing the commercial C. P. salt several times. Sodium metatungstate and barium chloride were then dissolved in water, heated to boiling and mixed in equivalent quantities. A portion of the tungsten and barium came down as a white precipitate; this was filtered out and the solution allowed to cool. During the cooling more of the white precipitate separated, and in many cases the whole tungsten content changed to the insoluble barium salt. In some instances, however, only a portion of the substance sustained this change. It was filtered out, and on further evaporation of the solution, crystals of barium metatungstate separated. In some of the preparations, the sodium metatungstate was made by the action of the electric current on the normal sodium salt. This material was furnished by Dr. Geo. E. Thomas.

The water content of the crystals was determined by heating the powdered salt in a porcelain crucible for one hour at a dull red heat. The results were varied. The salt appeared to be slightly efflorescent. The values obtained for the atomic mass of tungsten are more discordant than those obtained by Scheibler, and hence are of no particular value.

After decomposing the salt with aqua regia, the barium was determined as sulphate and the tungsten as trioxide. These results also varied too greatly for atomic mass determinations; they, however, approximated the generally accepted formula,



THE MOST PROBABLE VALUE OF THE ATOMIC MASS OF TUNGSTEN.

It would appear that all of the preceding methods for the determination of the atomic mass of tungsten are unsatisfactory. So far as known, there is no perfectly reliable method for the determination of this constant. The method of reduction and oxidation is probably more accurate than any of the other methods which have been employed. The results obtained by it vary about one unit, and even more in exceptional cases. The high values published by some experimenters are undoubtedly due to the volatilization of oxide. The mean of all the determinations is approximately 184. Until a more accurate means

has been devised for determining the atomic mass of tungsten, it will perhaps be better to accept the result 184, as the most probable value of this constant.

UNIVERSITY OF PENNSYLVANIA.

ON β -HEPTYLAMINE.^{1, 2}

[FIRST PAPER.]

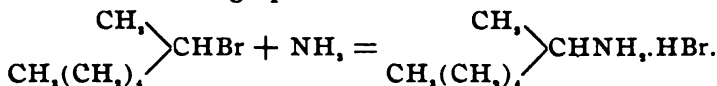
BY THOMAS CLARKE.

Received August 2, 1899.

ALTHOUGH β -heptylamine has been prepared by Cahours and Pelouse³ and later by Schorlemmer,⁴ the description of it was so meager, that it was considered worth while to study this base more thoroughly.

β -Heptyl bromide, prepared according to the method of Venable⁵ from heptane of the *Pinus sabiniana*, was heated in a sealed tube at 100° with an excess of an alcoholic solution of ammonia. The resulting products were primary β -heptylamine hydrobromide, ammonium bromide, heptylene, and unchanged β -heptyl bromide. There was no evidence of the formation of a base other than primary β -heptylamine, which accords with the observations of Jahn,⁶ that by the action of ammonia on isopropyl iodide, β -hexyl iodide or β -octyl iodide, only amide bases are formed. The formation of unsaturated hydrocarbons of the series C_nH_{2n} was observed by Jahn,⁷ in the action of ammonia on isopropyl iodide and β -hexyl iodide.

The results show that, similar to the examples cited from Jahn, two separate reactions take place in the action of ammonia on β -heptyl bromide. One is the condensation of the ammonia with the bromide to form the primary amine hydrobromide as shown in the following equation :



¹ I name those compounds which have the group or element characterizing them attached to the second carbon atom in the normal hydrocarbon chain, β -derivatives; thus $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHNH}_2\text{CH}_3$ is called β -heptylamine.

² Read at the Columbus meeting of the American Association for the Advancement of Science.

³ *Jsb. d. Chem.* (1863), 528.

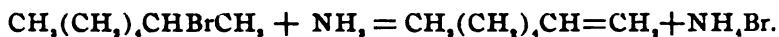
⁴ *Ann. Chem.* (Liebig), 127, 318.

⁵ *Ber. d. chem. Ges.*, 13, 1650.

⁶ *Monatsh. Chem.*, 3, 165.

⁷ *Ibid.*, 3, 166 and 170.

The other is the splitting off of hydrogen bromide by the ammonia with the formation of heptylene and ammonium bromide as follows :



Preparation of β -Heptylamine. $\text{CH}_3(\text{CH}_2)_5\text{CHNH}_2\text{CH}_3$.— β -Heptyl bromide, boiling-point 164° – 168° , was sealed in a tube with an excess of an alcoholic solution of ammonia and heated in a water-bath for forty-eight to seventy-two hours; at the end of this time the reaction was apparently complete. The contents of the tube were filtered to remove ammonium bromide, which had formed in some quantity. The alcohol was then distilled off and the residue heated for some time in a partial vacuum at about 125° in order to free it from unchanged β -heptyl bromide or other impurities volatile at that temperature and pressure. The crude β -heptylamine hydrobromide, obtained in this manner, was dissolved in a small quantity of warm benzene and petroleum ether added until the clear liquid was slightly turbid.

After warming on a water-bath until clear and allowing to stand for some hours, fairly pure β -heptylamine hydrobromide crystallized out. The purified hydrobromide was dissolved in a small quantity of water and an excess of potassium hydroxide solution (1 : 1) added. Although there was evolution of heat and the separation of the amine seemed complete, the mixture was heated fifteen minutes on a water-bath to be sure that all the base had been liberated. The free β -heptylamine, floating on the potash solution, was separated and the solution extracted with ether. After drying the ethereal solution with solid potassium hydroxide and distilling off the ether, a slightly brown colored liquid was obtained, which was distilled in a partial vacuum from anhydrous barium oxide, over which it had stood for five days. When carefully fractionated at ordinary pressures, the greater portion distilled at 142° – 144° (most at 143°). The density of this fraction at 24° compared with water at the same temperature is 0.7667.

On diluting the alcohol which was distilled from the crude hydrobromide, an oil separated. This was roughly divided by distillation into two fractions, the lower boiling being heptylene, as it had the characteristic odor, and absorbed bromine; the

higher boiling fraction was unchanged β -heptyl bromide as was shown by its boiling-point and the presence of bromine.

β -Heptylamine is a colorless liquid with a very characteristic amine-like odor and bitter, burning taste. It is soluble in alcohol, ether, or petroleum ether; slightly soluble in water. It takes up some water, from which it is freed with the greatest difficulty. It is strongly alkaline, combining with acids with evolution of much heat. If left in the air, it absorbs water and carbon dioxide.

I. 0.2317 gram of the amine gave 0.6166 gram carbon dioxide and 0.3140 gram water.

II. 0.1353 gram of the amine gave 15.5 cc. nitrogen at 28° and under a pressure of 752 mm.

III. 0.2844 gram of the amine gave 33 cc. nitrogen at 29° and under a pressure of 752 mm.

	Calculated for $C_7H_{17}N$.	I.	Found. II.	III.
Carbon	73.05	72.58		
Hydrogen	14.78	15.06		
Nitrogen	12.16		12.43	12.52

β -Heptylamine Hydrobromide, $CH_3(CH_2)_5CHNH_2CH_2.HBr$.—The fairly pure β -heptylamine hydrobromide as obtained in the preparation of β -heptylamine was recrystallized from a mixture of benzene and petroleum ether until the melting-point was constant.

β -Heptylamine hydrobromide crystallizes in exceedingly fine, white, silky needles, which are two to three cm. in length and melt at 163°. It is very soluble in alcohol, benzene, and water; soluble in a large volume of dry ether, practically insoluble in petroleum ether.

I. 0.3125 gram of the substance gave 0.2980 gram silver bromide.

II. 0.3988 gram of the substance gave 0.3836 gram of silver bromide.

	Calculated for $C_7H_{18}NBr$.	I.	Found. II.
Bromine	40.81	40.57	40.93

β -Heptylamine Hydrochloride, $CH_3(CH_2)_5CHNH_2CH_2.HCl$.—This salt was prepared by passing hydrochloric acid gas into an ethereal solution of β -heptylamine. As the ether was not com-

pletely dry, it did not all precipitate as was expected, therefore the ether was allowed to evaporate. The slightly colored residue, obtained in this manner, was dissolved in warm benzene, petroleum ether added until slightly turbid, and set aside to crystallize. Crystallization was repeated until the melting-point was constant.

β -Heptylamine hydrochloride crystallizes in beautiful, white, silky, slightly deliquescent needles, which melt at 133° . It is readily soluble in water, alcohol, and benzene; insoluble in petroleum ether and sparingly soluble in ether.

I. 0.2198 gram of the substance gave 0.4460 gram carbon dioxide and 0.2322 gram water.

II. 0.1928 gram of the substance gave 15.4 cc. nitrogen at 19° and under a pressure of 753 mm.

III. 0.2029 gram of the substance gave 18 cc. nitrogen at 19° and under a pressure of 753 mm.

IV. 0.3345 gram of the substance gave 0.3140 gram silver chloride.

V. 0.3618 gram of the substance gave 0.3370 gram silver chloride.

	Calculated for $C_7H_{15}NCl$.	I.	II.	Found. III.	IV.	V.
Carbon	55.45	55.35				
Hydrogen	11.88	11.74				
Nitrogen	9.24		8.88	9.87		
Chlorine	23.43				23.21	23.09

β -Heptylamine Chlorplatinate, $(C_7H_{15}NH_2 \cdot HCl) \cdot PtCl_4$, was prepared from the amine hydrochloride by dissolving it in a small amount of water and adding an excess of chlorplatonic acid. The salt separates in fine plates which are sparingly soluble in cold, easily in warm water. It crystallizes from the latter on cooling, in large yellow plates. It is readily soluble in alcohol. On heating to 195° it decomposes.

0.2164 gram of the salt gave 0.0653 gram platinum.

	Calculated for $C_{14}H_{34}NCl_4Pt$.	Found.
Platinum	38.23	37.98

β -Heptylamine Chloraurate, $C_7H_{15}NH_2 \cdot HClAuCl_4$, was prepared by adding chlorauric acid to a concentrated solution of the

amine hydrochloride in water. It separates in light yellow crystals which melt at 63° – 64° . In cold water it is sparingly soluble; readily soluble in warm water from which it may be crystallized in large yellow plates.

0.1805 gram of the salt gave 0.0778 gram gold.

Gold	Calculated for $C_7H_{17}NCl_4Au$.	Found.
	43.30	43.10

β -Heptylamine Oxalate, $(C_7H_{17}NH_2)_2C_2H_2O_4$, was prepared by adding the amine in slight excess to an alcoholic solution of oxalic acid, precipitating with ether, and recrystallizing from alcohol. It crystallizes in beautiful, white plates, which melt at 204° – 205° with decomposition. In cold water or alcohol it is moderately soluble; in the warm solvents it is readily soluble. It is insoluble in ether and petroleum ether. On boiling it with water it is completely decomposed, the oxalic acid remaining and the β -heptylamine passing off with the steam.

I. 0.2545 gram of the substance gave 0.5626 gram carbon dioxide and 0.2605 gram water.

II. 0.1873 gram of the substance gave 0.4122 gram carbon dioxide and 0.1882 gram water.

III. 0.2900 gram of the substance gave 24.8 cc. nitrogen at 18° and under a pressure of 753 mm.

IV. 0.2658 gram substance gave 20.7 cc. nitrogen at 18° and under a pressure of 753 mm.

	Calculated for $C_{18}H_{36}O_4N_2$.	I.	II.	Found.	III.	IV.
Carbon	60.00	60.30	60.03			
Hydrogen	11.25	11.37	11.17			
Nitrogen	8.75				8.35	8.90

At the time I made the nitrogen determinations given in this paper, the apparatus was inadequate, which will, in part, account for the poor results obtained.

The study of β -heptylamine is being continued in this laboratory.

I wish to express my sincere thanks to Dr. F. P. Venable for his advice and interest in the prosecution of this task.

THE AMOUNT OF HUMUS IN SOILS AND THE PERCENTAGE OF NITROGEN IN THE HUMUS, AS AFFECTED BY APPLICATIONS OF AIR-SLAKED LIME AND CERTAIN OTHER SUBSTANCES.

BY H. J. WHEELER, C. L. SARGENT, AND B. L. HARTWELL.

Received August 14, 1899.

It is a well-known fact that lime, under favorable conditions, hastens the decomposition of organic matter. Notwithstanding this fact, however, lime is a most beneficial substance to apply to certain soils if used in rational quantities in connection with other manures, and provided such a system of manuring and cropping is employed that a sufficient supply of humus is maintained whether by the use of stable manure, muck, green manures, or by the occasional turning under of a grass sod.

In consideration of the interesting observations by Hilgard and Jaffa,¹ showing that the nitrogen content of the humus of certain soils of the arid regions of the United States exceeded in several instances eighteen per cent., and in view of the idea advanced later² by Hilgard to the effect that the nitrogen percentage of the humus may probably be taken as an indication of the degree of immediate assimilability of the nitrogen of soils, it seemed desirable to make a study of our own soil in its natural state and as affected by liming. The surface soil employed in this experiment came from plot OO of the cooperative acre located between fields B and C, and the subsoil was taken at the north end of the series of plots of which plot OO formed a part.³ The surface soil and subsoil were each thoroughly mixed before being placed in the pots. The pots employed were galvanized iron ash-cans about twenty-six inches deep, and eighteen inches in diameter with bottoms inclined toward the center, at which point an opening was left to insure drainage. The pots were set into the soil to within two inches of the tops and agricultural drain tiles laid underneath, to prevent the ingress of surrounding soil-water. One hundred and fifty-four pounds of subsoil, and 100 pounds of surface soil were placed in each pot.

¹ *Agricultural Science*, 8, 165 (1894).

² Bulletin 47, U. S. Department of Agriculture, Division of Chemistry, pp. 58-60.

³ See chart of experimental plots, Ninth Annual Report, Rhode Island Agricultural Experiment Station (1896).

The pots were filled in the spring of 1893. In 1893 and 1894 each manured pot received 7.36 grams of potassium chloride and 22.07 grams of dissolved bone-black. In the succeeding years, these amounts were increased to ten and twenty-five grams respectively. Wherever nitrogen was applied, it was at the rate of 2.65 grams per pot. Lime, unless otherwise specified, was applied in the form of air-slaked lime, practically free from magnesia, at the rate of 147.2 grams per pot (four tons per acre). Gypsum was applied so as to furnish the same amount of calcium oxide as the air-slaked lime at the rate of four tons per acre. Rhode Island capped corn (maize) was grown in the pots in 1893, oats in 1894, and spring rye in 1895. The soil employed in making the determinations was removed from the pots late in the autumn of 1895, or some weeks subsequent to the harvesting of the rye. In the case of pots which had been manured alike, approximately like amounts of soil were taken from each, and the samples for analysis were then taken from the mixture of these lots.

The following were the methods of analysis employed in the determination of humus and nitrogen in the humus: Humus was determined by first extracting the soil (twenty grams) with dilute hydrochloric acid as proposed by Hilgard,¹ but with the employment of an automatic washing apparatus, until no further reaction for lime was obtainable in the wash solution. The acid was then removed by successive washings with water until the wash-water was neutral.

In the subsequent treatment with ammonia, the Huston and McBride,² modification of the Grandeau method was employed. By this modification, the time of treatment and relation between volume of solvent and the quantity of material extracted, are constant factors. This seemed to be desirable in comparative tests, of the character under consideration. Successive extractions as proposed by Snyder³ would undoubtedly have given even greater percentages of extract, since many extractions are necessary in the case of our upland soils to remove everything which can be dissolved by ammonia. It is not improbable, however, that a portion of the more insoluble extract may not be

¹ Wiley's Principles and Practice of Agricultural Analysis, Vol. I, p. 325.

² Wiley's Principles and Practice of Agricultural Analysis, Vol. I, pp. 327-328.

³ Annual Report Minnesota Agricultural Experiment Station, 1893, pp. 251-252.

strictly humus, but may consist of unhumified matter extracted by the ammonia from plant residues.

The nitrogen in the humus was determined by using a two and one-half per cent. solution of potassium hydroxide in place of the solution of ammonium hydroxide of like strength, which was employed in the determination of humus. Aliquot portions of the extract were then neutralized with sulphuric acid, and after evaporating to dryness in a Kjeldahl flask, the nitrogen was determined as usual by the method of Kjeldahl. The soils were air-dried before analyzing, and the different samples contained from 2.00 to 2.75 per cent. of water, determined at 100° C. The following are the analytical results obtained, calculated to percentages of *dry* soil.

Nos. of pots.	Manures applied. ¹	Humus nitrogen in dry soil.	Humus in dry soil.	Nitrogen in dry humus.
21	Unmanured.....	0.130	3.86	3.37
16, 18, 25	Ammonium sulphate.....	0.128	3.93	3.26
15, 22	Ammonium sulphate, air-slaked lime (1 ton per acre)	0.133	3.77	3.53
17, 19, 26	Ammonium sulphate, air-slaked lime (4 tons per acre)	0.126	3.63	3.47
1, 8	Ammonium sulphate, calcium sulphate (land plaster) at a rate equivalent in CaO to 4 tons of air-slaked lime per acre.....	0.139	3.65	3.81
20, 27	Without nitrogen and lime...	0.129	3.75	3.44
23, 24	Air-slaked lime (4 tons per acre).....	0.139	3.51	3.68
6, 13	Sodium nitrate	0.143	3.93	3.64
7, 14	Sodium nitrate and air-slaked lime (4 tons per acre)	0.133	3.42	3.89

A study of the foregoing table reveals certain points of interest. Comparing the result from the pot which was unmanured (21), with that from those pots where potash and phosphoric acid were applied annually (20 and 27), it will be seen that the humus nitrogen and the percentage of humus had become but slightly less where the manures were applied, than in the unmanured soil, while the percentage of nitrogen in the dry humus showed also but slight variation.

¹ All of the pots except No. 21, received like amounts of potash and phosphoric acid.

By a comparison of the result where potash and phosphoric acid were employed (20 and 27), with that from the pots which received an additional application of lime (23 and 24), it appears that where lime was applied, the humus nitrogen in the soil had increased, and the percentage of humus had decreased 0.24 per cent., while the percentage of nitrogen in the humus had been augmented by 0.24 per cent.

In the case of the pots receiving nitrogen as sodium nitrate (6, 13, 7, and 14), it will be seen that the percentage of humus nitrogen was lower in the limed ones (7 and 14), and the humus was 0.51 of a per cent. lower but the percentage of nitrogen in the humus itself was 0.25 per cent. higher.

From an inspection of the results from the limed and unlimed ammonium sulphate pots (16, 18, 25, 15; 22, 17, 19, and 26), it will be seen that where lime was applied at the rate of one ton per acre (pots 15 and 22), the humus nitrogen was slightly greater, the humus was 0.16 per cent. less, and again the percentage of nitrogen in the humus itself was 0.27 per cent. greater.

In the case of the pots receiving lime at the rate of four tons per acre (pots 17, 19, and 26), no decided variation in the amount of humus nitrogen resulted, though the percentage of humus was found to be three-tenths per cent. less than where no lime was used, and, as in each of the other cases cited, the percentage of nitrogen in the humus was increased by liming.

Where calcium sulphate (gypsum or land plaster) was applied (pots 1 and 8), so as to furnish an amount of calcium oxide equivalent to that supplied by the air-slaked lime at the rate of four tons per acre, the humus nitrogen was 0.011 of a per cent. higher than where neither lime nor gypsum was applied (pots 16, 18, and 25), the humus was 0.28 of a per cent. lower, and the percentage of nitrogen in the humus 0.55 per cent. higher.

From the foregoing it will be seen that without exception the addition of air-slaked lime or gypsum resulted in lowering the total amount of humus, as compared with the unmanured plot, yet in every instance the percentage of nitrogen in the humus had been increased. In fact the latter statement applies also even where no nitrogen was added (pots 23 and 24).

Where lime was not applied, but nitrogen was employed in form of ammonium sulphate, which in the acid soil proved

poisonous to plants (pots 16, 18, and 25), it will be observed that the percentage of nitrogen in the humus was even less than where no manure was used (pot 21). On the contrary, where nitrogen in the form of sodium nitrate, was added without lime (pots 6 and 13), the percentage of nitrogen in the humus was greater than in the case of the unmanured soil (pot 21).

It is also of special interest to observe that in the case of the unlimed soil which received potash and phosphoric acid, but no nitrogen (pots 20 and 27), the percentage of humus became less than in the unmanured soil, while on the contrary, where nitrogen was applied as sodium nitrate, and as ammonium sulphate, to unlimed soil, it is possible that a slight increase in the percentage of humus resulted. The differences are not great enough, however, to furnish any positive evidence in this respect.

From what has preceded, in relation to the percentage of nitrogen in the humus, it seems probable, in case the view of Hilgard is correct, that the use of lime had actually increased the immediate assimilability of the humus nitrogen, notwithstanding the fact that the heaviest crops were produced by the limed pots. This is especially interesting in view of the fact that Hilgard and Jaffa¹ in twelve years' continuous cropping with grass upon soil of the California Station, found an increase of two-tenths per cent. in humus, but a decrease of nitrogen in the humus from eighteen to three per cent.

Lime has, as shown, decreased the percentage of humus, yet this has been in the case of continuous culture of cereals. In consideration, however, of the wonderful increase of roots and residual organic matter in our limed soils when they are seeded to grass, as compared with those which are unlimed, and since lime is well known to facilitate the humification of organic matter within the soil, there appears to be no danger of impoverishing the soil humus by the reasonable use of lime, wherever the land is occasionally left in grass for a few years, or where the supply of organic matter is maintained by the use of sufficient muck, stable manure, or by plowing in an occasional green crop. It is of considerable interest to note, where lime was applied, that notwithstanding the fact that the total humus was reduced, the percentage of nitrogen in the humus was increased in every case. However, this is in accord with the conditions which pre-

¹ Bulletin 47, U. S. Department of Agriculture, Division of Chemistry, 1895, p. 59.

vail generally where plant residues undergo decay. Hydrogen and oxygen are eliminated as water and carbon dioxide, more rapidly than nitrogen is eliminated.

Where sodium nitrate was applied without the use of lime, the percentage of humus nitrogen was greatest of all and the percentage of humus reached its maximum. The nitrogen in the humus was also two-tenths per cent. above that where nitrogen and lime were omitted (pots 20 and 27), and 0.27 per cent. above that where no manure was used (pot 21). This is particularly interesting in view of the fact that the unlimed sodium nitrate pots produced each season greater crops than pot 21, 20, or 27. These data indicate, therefore, a storage of some of the nitrate nitrogen within the soil in the form of organic matter,¹ which becomes quickly soluble in ammonium hydroxide, or, in other words, passes largely into a condition which permits of its classification with that organic complex which is termed humus.

In the light of recent investigations, it is probable that this may be accomplished by means of the denitrifying organisms which, while liberating some of the nitrogen in the gaseous state, may nevertheless store a portion in the soil in organic combinations. This view is also supported by the fact that lime decreases the activity of the denitrifying organisms, and that no such marked indications of the storage of nitrate nitrogen were observed where lime was employed. At all events, if these indications are verified by future investigations, it would seem probable that the disappearance of the nitrate nitrogen from a soil may not indicate the total loss of the nitrogen by cropping, drainage, and by elimination as gas, but that, under certain conditions, some portion of it at least may be transformed into a more stable form, which will subsequently become gradually available to plants.

It is to be regretted that opportunity has not been afforded to determine the total nitrogen content of the soils, together with the relative amounts of ammonium compounds, nitrates, and nitrites. It is hoped, however, that further time and means will become available in order that these interesting questions can be more extensively and thoroughly studied.

LABORATORY OF THE RHODE ISLAND
AGRICULTURAL EXPERIMENT STATION.

¹ Berthelot records a similar observation and concluded that it was due to purely chemical processes or to the activity of micro-organisms. *Compt. rend.*, 106, 638 (1888), abs. in *Chem. Centrbl.*, p. 486 (1888), cited from *Jsb. Agriculturchemie*, p. 22 (1888).

NOTE ON THE COLOR OF CHLORINE SOLUTIONS.

BY E. H. SARLES.

Received August 7, 1899.

SOME time ago it was noticed that upon passing chlorine into ethyl alcohol to make chloral, the liquid finally separated into a lower yellow layer, and an upper green layer. The upper layer was a grass-green, not a yellowish green.

It seems therefore that chlorine can dissolve with a green color as well as with the usual yellow color. This fact has apparently been overlooked, for a considerable search through the chemical literature has revealed no record of a green-colored solution of chlorine; the matter seemed therefore worth looking into.

Litmus paper was immediately bleached by the green liquid but, upon blowing air through to remove uncombined chlorine, the bleaching power disappeared, the liquid losing its green color and giving simply an acid reaction. The color also disappeared upon passing carbon dioxide through the green liquid and upon standing for several hours exposed to the air. These facts would indicate a true solution of chlorine, chloral, chloroform, carbon disulphide, all giving yellow-colored solutions; no trace of green was observed by the naked eye.

After fractionating the green liquid and passing chlorine into the fractions, the green color reappeared only in the fractions boiling below 94°C ., but the result was not satisfactory as the color of the fraction had lost much of the original green brilliancy. This indicates that the solvent is either easily decomposed or that it is very volatile, and that consequently only a small part is caught on distilling. This indication is strengthened by the fact that after several fractionations, the green color is lost entirely and cannot be regained on adding chlorine.

Considerable time has been spent in seeking the conditions most favorable to the formation of the green solution. The best results have so far been obtained by cooling the alcohol to about -15°C . with ice and crystallized calcium chloride while passing chlorine in. These results are preliminary; I intend to carry the investigation to some conclusion and hope to be able to announce the result soon.

RUTGERS COLLEGE,
August 5, 1899.

IMPROVEMENT IN THE CHEMICAL COMPOSITION OF THE CORN KERNEL.¹

BY CYRIL G. HOPKINS.

Received August 25, 1899.

THE many different uses which are made of corn and the enormous value of the crop to the United States may certainly be deemed sufficient reason for investigating the possibility of making improvements in the chemical composition of this important grain. The nature of any desired improvement will, of course, depend upon the use which is to be made of the crop produced. For example, if corn is grown for the manufacture of starch, glucose-sugar, sirup, or alcohol, it is desirable that the grain contain a high percentage of carbohydrates, and that the percentages of its other chief constituents, protein and fat, should be reduced as much as possible. If corn is used as feed for growing animals, or manufactured into corn flour for human food, a higher percentage of protein will certainly increase its value. If it is to be used chiefly for fattening stock, an increased percentage of fat might be the improvement to be desired. That the chemical composition of corn can be changed seems reasonably probable from the changes which have been produced in some other plants,—notably in the sugar-beet.

Before the work reported in this paper could be begun, it was found necessary to make a chemical study of the corn plant, and to devise methods for conducting experiments with the object of improving the composition of the grain. It is known that the mineral content of plants can be changed to some extent by the addition to the soil of mineral materials in a form readily available to the plant, but that the temporary change thus effected would have any appreciable hereditary tendency seems very unlikely. The method of procedure which seemed most promising is based upon the common method of making improvement in animals; namely, selecting the best examples of the desired type and breeding successively and under the best conditions from that stock, retaining from each generation only the highest types obtained. This is practically the method by which the

¹ Read before the American Chemical Society at the Columbus meeting held on August 21 and 22, 1899. This is an abstract from advance sheets of a bulletin on this subject, which will be published by the University of Illinois Agricultural Experiment Station as Bulletin No. 55, which will give the full data and details of these experiments.

sugar content of certain varieties of beets has been increased from less than five per cent. to twelve or even to sixteen per cent. A small portion of a beet is analyzed and, if it is found to be sufficiently rich in sugar, the beet is then set out, or planted, as a "mother," or seed, beet. From the seed produced beets are grown and another selection of seed beets is made on the basis of their sugar content. But the kernel of corn is not sufficient in quantity to make a complete chemical analysis by any practical method, and certainly the same kernel could not be used for analysis and also for seed.

Early in the year 1896 the writer began a special study of the chemistry of corn. Among the important facts indicated by the results obtained at that time were the following :

1. That the ear of corn is approximately uniform throughout in the composition of its kernels.
2. That there is a wide variation in the chemical composition of different ears of the same variety of corn.

That these conclusions are correct has been fully shown by some more recent work.¹ Approximate uniformity in the composition of the kernels, or grain, from the individual ear of corn has been established by the concordant evidence of a large number of analyses of parts of ears, and of many ash determinations and protein determinations in single kernels of corn. This may be illustrated by quoting the percentages of protein found in ten different kernels from each of two different ears :

High-protein ear.		Low-protein ear.	
Kernel No.	Protein.	Kernel No.	Protein.
1	12.46	1	7.45
2	12.54	2	7.54
3	12.44	3	7.69
4	12.50	4	7.47
5	12.30	5	7.74
6	12.49	6	8.70
7	12.50	7	8.46
8	12.14	8	8.69
9	12.14	9	8.86
10	12.71	10	8.10

The following *highest* and *lowest* percentages of the more important constituents of the corn kernel, found in analyzing fifty different ears of a single variety of corn, may serve to illus-

¹ For complete data see University of Illinois Agricultural Experiment Station, Bulletin 53, 150-157 (1898).

trate the wide variation in the composition of corn from different ears :

	Ash.	Protein.	Fat.	Carbohydrates.
Maximum.....	1.74	13.88	6.02	85.79
Minimum	1.09	8.35	3.95	78.92
Difference	0.65	5.53	2.07	6.87

With every constituent the variation is greater than Flechig¹ found with thirteen different varieties, and it is nearly as great as found by the Connecticut Experiment Station² with about seventy-five different varieties of corn grown under ninety presumably different conditions.

The uniformity of the individual ear of corn makes it possible to determine very approximately the composition of the grain by analyzing a sample consisting of a few rows of kernels from the ear. The remainder of the kernels of the ear may then be planted if desired. The wide variation in composition between different ears is a very important factor in the work of selecting seed, as a starting-point is thus furnished in each of the several lines of desired improvement.

The general plan³ of the experiments to improve the chemical composition of corn was to make analyses of samples from a large number of ears, select for seed those ears which were found to contain a high percentage of the desired constituent, plant in an isolated field (to avoid cross fertilization from other corn), and grow the crop under as good field conditions as possible. From the crop obtained a large number of ears are selected, and samples of each ear are analyzed, seed being taken, as before, from those ears which are found to be highest in the percentage of the constituent which it is desired to increase. Each year this process is repeated. While it may require ten or twenty years' work to enable one to form a very definite opinion as to the extent to which it is possible to influence the chemical composition of corn, it is believed that the data and results thus far obtained may be of practical and scientific interest.

¹ Landwirtschaftliche Versuchs-Stationen, 32, 17 (1886).

² Connecticut Agricultural Experiment Station, Annual Report (1893).

³ All work reported in this paper was done upon a single variety of corn, commonly known as Burr's White. It has been grown for several years by the Illinois Agricultural Experiment Station with precautions to keep the variety pure and distinct. The analytical methods employed in the work herein reported have been described in detail in Bulletins 43 and 53 of the Illinois Station. All results are reported on the basis of dry matter, or water-free substance.

From the 1896 crop of Burr's White corn grown upon the Illinois Experiment Station farm, two bushels, or 163 ears, of good sound ear corn, suitable for seed, were selected. From each ear a sample consisting of three rows of kernels, lengthwise of the ear, was taken for analysis. From this lot of 163 ears, four different sets of seed corn were selected on the basis of chemical composition:

1. A set of twenty-four ears, each of which contained a high percentage of protein.
2. A set of twelve ears, whose percentage of protein was comparatively low.
3. A set of twenty-four ears, found to contain a high percentage of fat.
4. A set of twelve ears, containing a low percentage of fat.

Plans were made to carry on separately four direct experiments to change the chemical composition of corn; namely, (1) to increase the percentage of protein, (2) to decrease the protein, (3) to increase the fat, and (4) to decrease the fat. It is, of course, manifest that if the percentages of both protein and fat are increased, the percentage of carbohydrates must necessarily be decreased, and *vice versa*. By planting plots with both high-protein and low-protein corn, or with both high-fat and low-fat corn, results may be obtained which show the influence of selected seed, as independent and distinguishable from the effects due to the influence of the season.

In the spring of 1897 the four sets of corn which had been selected were planted on four different fields, or plots, each of which was fairly well isolated from other corn fields in order to avoid cross fertilization by corn of different chemical composition. For convenience these four plots are called: 1. High-protein plot; 2. Low-protein plot; 3. High-fat plot; 4. Low-fat plot. Invariably the seed planted in each row was all taken from a single ear; so that the high-protein plot, for example, contained twenty-four rows planted with seed from the twenty-four ears selected for that purpose. In the high-protein and high-fat plots the seed containing the very highest percentage of the desired constituent was planted in the middle rows, the remainder of the seed being planted in approximately uniform

gradation to either side. In the low-protein and low-fat plots the seed containing the very lowest percentages of protein and fat, respectively, was planted in the middle rows. This arrangement may be clearly seen by referring to the tables. The plots were given ordinary cultivation, and a good crop of corn was grown on each. When the corn was harvested a set of ten good ears was selected from each row, excepting from some outer rows. From some of the middle rows duplicate sets of ten ears each were taken from the same row, as will be seen from the tables, the analytical data from such rows being given in duplicate in all cases. Two rows of kernels (lengthwise of the ear) were taken from each of the ten ears and mixed to form a composite sample for analysis to represent the good corn grown on each row in the plots.

EXPERIMENTS TO INFLUENCE THE PROTEIN IN CONTENT OF CORN.

The results from the experiments to change the percentage of protein in corn will be first considered. The following tables are arranged to show the percentage of protein in the dry matter of the seed planted and the crop produced in 1897. For reference, the laboratory serial numbers of all samples whose analyses are herein shown are also given.

TABLE 1.—PROTEIN IN CORN PLANTED AND HARVESTED ON HIGH-PROTEIN PLOT IN 1897.

Plot row No.	Corn planted.		Corn harvested.	
	Corn No.	Protein. Per cent.		Protein. Per cent.
1	94	11.89	270	9.61
2	86	12.07	275	11.07
3	230	12.10	280	10.94
4	213	12.40	285	11.48
5	100	12.28	290	10.85
6	119	12.38	295	11.64
7	227	12.63	300	11.46
8	153	12.51	305	11.57
9	175	12.68	310	11.17
10	84	12.79	315	11.14
11	110	12.81	320	11.16
12	126	13.87	{ 325	11.60
			{ 330	11.31
13	92	12.96	{ 335	11.07
			{ 340	11.44

Plot row No.	Corn planted.		Corn harvested.	
	Corn No.	Protein. Per cent.	Corn No.	Protein. Per cent.
14	177	13.06	{ 345	10.89
			{ 350	10.67
15	188	13.10	{ 355	10.34
			{ 360	11.48
16	232	12.76	365	11.05
17	87	12.40	370	10.75
18	204	12.57	375	10.86
19	105	12.36	380	11.07
20	141	12.42	385	10.88
21	172	12.28	390	11.73
22	222	12.34	395	10.76
23	147	12.21	400	11.30
24	208	12.05	405	11.53
Plot averages,		12.54	11.10	

TABLE 2.—PROTEIN IN CORN PLANTED AND HARVESTED ON LOW-PROTEIN PLOT IN 1897.

Plot row No.	Corn planted.		Corn harvested.	
	Corn No.	Protein. Per cent.	Corn No.	Protein. Per cent.
1	151	9.31
2	114	9.12	410	10.55
3	83	9.08	415	10.89
4	225	9.15	420	10.26
5	116	8.38	425	10.10
6	145	8.25	{ 430	10.73
			{ 435	9.90
7	99	8.40	{ 440	10.36
			{ 445	10.20
8	215	9.22	450	9.89
9	185	9.33	455	10.24
10	164	9.36	460	11.20
11	113	9.30	465	12.24
12	193	9.47
Plot averages,		9.03	10.55	

The average composition of the corn from the high-protein plot shows a protein content of 11.10 per cent., while 10.55 is the average percentage of protein in the corn from the low-protein plot, indicating that the difference, 0.55 per cent., may be ascribed to the influence of the seed selection. On account of the plan, or order, in which the seed corn was arranged in the plots, that is, with the corn of highest protein content in the central rows of the high-protein plot, and the corn of lowest pro-

tein content in the central rows of the low-protein plot, we might expect to find a somewhat wider average difference in protein content if we consider only the corn grown on the central half of each plot. From rows 7 to 18 of the high-protein plot we find the average protein content of the corn produced to be 11.12 per cent., while 10.21 is the average percentage of protein in the corn from rows 4 to 9 of the low-protein plot, thus showing an average difference of 0.91 per cent.

From each set of ten ears from the 1897 crop, four of those which appeared most suitable for seed corn were reserved for further use. From each of these ears a sample consisting of three or four rows of kernels was taken for analysis. In order to retain hereditary influences the seed for the high-protein plot for 1898 was all selected from corn which grew from seed of high-protein content the previous year. On this account corn with high-protein content from the low-protein plot was rejected for seed. Likewise seed for 1898 for the low-protein plot was selected only from corn which grew upon that plot in 1897.

In conducting the experiments in 1898 the same general plan of the previous year was followed, and the results obtained were nearly the same as in 1897, and the data obtained from the high-protein and low-protein plots will not be given in this paper.

In order to avoid local differences in the soil conditions, a third plot of ground was planted in 1898 with corn of known protein content. For want of a better name this is called the "mixed-protein plot." It contained five rows of ten hills each. In each hill were planted four kernels of corn of which two were high and two were low in protein content. The kernels were so arranged in the hill that the stalk of corn produced from each could be known. When the crop was harvested eight to ten ears from both the high-protein seed and the low-protein seed were taken from each row. By taking two rows of kernels from each ear ten composite samples were made, of which five represent the corn grown from the high-protein seed, in the five rows, and the other five represent the corn produced in the same rows from the low-protein seed. The following table shows the protein content of the seed planted and of the samples taken from the crop harvested.

TABLE 3.—PROTEIN IN CORN PLANTED AND HARVESTED ON MIXED-PROTEIN PLOT IN 1898.

Plot row No.	Corn planted.		Corn harvested.		Corn planted.		Corn harvested.	
	Corn No.	Protein. Per cent.	Corn No.	Protein. Per cent.	Corn No.	Protein. Per cent.	Corn No.	Protein. Per cent.
1	408	12.80	698	11.24	446	8.84	697	9.72
2	326	13.62	700	11.75	458	8.22	699	11.04
3	407	12.72	702	12.10	427	8.29	701	10.09
4	304	11.97	704	11.65	416	8.88	703	10.89
5	364	11.89	706	11.81	448	9.05	705	10.58
Plot averages,				11.71	10.46			

The results of analysis show that in every row the high-protein seed produced corn with a higher protein content than that produced by the low-protein seed. The average protein content of the corn from the high protein seed is 11.71 per cent., while 10.46 is the average percentage of protein in the corn from the low-protein seed. This makes an average difference of 1.25 per cent. of protein which is attributable without question solely to the selection of seed on the chemical basis.

Incidentally it may be stated that the writer has found different ears of good sound Burr's White corn varying from 7.50 per cent. to 16.11 per cent. of protein in the dry matter. The fact that one good ear of corn with a protein content above 16 per cent. has been produced is a promise of the possibility of improving corn in that direction. Indeed, it is but reasonable to suppose that this limit may be reached again or even exceeded, and very possibly with corn in larger amounts than single ears.

Combined chemical and mechanical studies of the corn kernel have been reported by Salisbury,¹ Haberlandt and Lenz,² Atwater,³ Voorhees,⁴ and Balland.⁵ The results obtained⁶ show that the protein in the corn kernel is contained principally in the glutinous layer surrounding the main body of the kernel. This layer is very thin at the crown of the kernel but quite thick at the sides. The germ in the center of the tip end of the kernel is also rich in protein, although the entire germ constitutes

¹ Trans. N. Y. State Agricultural Society, 8, 678 (1848).

² *Allgemeine land- und forstwirtschaftliche Zeitung*, 257 (1866); Hoffmann; *Jsb. Agricultur-Chemie*, 9, 106 (1866).

³ Thesis, Yale College (1869); *American Journal of Science and Arts* [2], 48, 352 (1869).

⁴ New Jersey Agricultural Experiment Station, Bulletin 105 (1894).

⁵ *Compt. rend.*, 122, 1004 (1896).

⁶ University of Illinois Agricultural Experiment Station, Bulletin 53, 138-140 (1898).



Fig. 1.

only about twelve per cent. of the kernel. The starchy portion, lying between the germ and the glutinous layer, consists almost entirely of carbohydrates, although the glutinous layer contains also a large percentage of carbohydrates.

On the basis of this knowledge of the general structure of the corn kernel and chemical composition of its several parts, the writer has made some investigations as to the possibility of selecting corn of high-protein content and of low-protein content by purely mechanical means, and has found that such a method is both possible and practicable. By making cross sections and longitudinal sections of several kernels from an ear of corn, one can judge with a very satisfactory degree of accuracy whether the corn is rich or poor in protein.

The illustration (Fig. 1) here shown was made from a photograph taken of the corn kernels and sections with a magnification of three diameters. At the left are two sections and a whole kernel from an ear of corn which contained 14.92 per cent. of protein. The sections and whole kernel at the right are from an ear containing 7.76 per cent. of protein. About one-fourth of the kernel was cut off from the tip end in making the cross sections. In the longitudinal sections the tip end of the kernel points upward to the right. It will be seen that in the cross sections the white, starchy layer nearly disappears in the high-protein corn but becomes very prominent in the low-protein corn. In the longitudinal sections this difference is also apparent, the white starch in the high-protein corn being confined almost entirely to the crown end of the kernel, while in the low-protein corn it extends into the tip in considerable amount. The germ in the high-protein corn is somewhat larger. This is also indicated by the size of the depressions in the whole kernels.

As an experiment about 300 ears of corn were examined by this mechanical method. Eighteen ears in the lot were picked out as possessing the physical characteristics which indicate a comparatively high content of protein, fifteen other ears which appeared to be low in protein being selected at the same time. Table 4 shows the results in detail, the percentage of protein in the corn from each ear being given as previously determined by chemical analysis.

TABLE 4.—ACTUAL PROTEIN CONTENT OF CORN SELECTED BY MECHANICAL EXAMINATION.

Ear No.	Corn selected for	
	High protein. Per cent.	Low protein. Per cent.
1	11.47	11.48
2	12.04	9.06
3	9.69	9.90
4	11.78	9.15
5	11.65	9.67
6	11.38	10.11
7	11.64	9.11
8	11.22	10.25
9	11.97	8.63
10	11.94	9.63
11	10.96	8.61
12	10.83	10.95
13	11.87	11.27
14	10.21	9.36
15	11.71	10.25
16	11.59
17	12.31
18	10.54
Averages, 11.38		9.83

The average protein content of the eighteen ears selected for high-protein corn is 11.38 per cent., while 9.83 is the average percentage of protein in the fifteen ears selected for low-protein corn. The examination consists in simply cutting cross sections and longitudinal sections from the kernels with a pocket-knife and judging as to the combined amount of glutinous layer and germ in relation to the quantity of white starchy matter, the observation being made with the naked eye. In making the selections the time given to each ear was about half a minute, and it is not assumed that the writer possesses any special skill in the art of judging the comparative sizes of small areas, or surfaces, the chief point involved in making these examinations. It seems but fair to suppose that the average corn-grower could, with some practice and care, make a better selection than is here shown. The selections shown in Table 4 were made from material¹ which was at hand and for the purpose of showing the

¹ NOTE.—The percentage of protein in the different ears in this plot of corn did not vary as much as would ordinarily be the case, because thirty-four of the ears highest in protein, and twenty-six of those lowest in protein, had previously been removed from this stock of corn, having been selected by chemical analysis.

feasibility of the method, rather than the extent to which it may be carried.

EXPERIMENTS TO INFLUENCE THE FAT CONTENT OF CORN.

From the lot of 163 ears of corn from the 1896 crop, to which reference has already been made, seed was selected for the high-fat and low-fat plots for 1897. Good crops of corn were grown, and when harvested composite samples of corn from the different rows were taken and analyzed. The results obtained¹ indicate that the fat content of corn is influenced very markedly by selecting seed according to its percentage of fat. The difference between the average percentages of fat in the corn from the two plots is 0.67 per cent., the average from the high-fat plot being 4.73 and that from the low-fat plot 4.06 per cent. of fat. There is a difference of 0.79 per cent. of fat between the averages of the two crops if we consider only the central half of each plot. It is noteworthy that the lowest percentage of fat in the corn from any row of the high-fat plot is higher than the highest percentage obtained from any row in the low-fat plot.

From each set of ten ears from the 1897 crop four ears were taken for individual analysis, a sample of three or four rows of kernels (lengthwise of the ear) being taken from each ear for this purpose. For 1898 the seed for the high-fat plot was all from corn which grew from high-fat corn in 1897, twenty-four ears being selected. For the low-fat seed twelve ears were taken from the corn which grew from low-fat seed in 1897. The system of planting the highest of the high-fat seed and the lowest of the low-fat seed in the central rows of the respective plots was followed in 1898. Good crops of corn were grown, and when harvested sets of ten ears each were taken from each row, composite samples to represent each row being made, as before, by taking two rows of kernels from each of the ten ears. Tables 5 and 6 give the percentage of fat in the seed planted and in the crop produced, for each row of corn.

¹ The complete data are not given in this paper.

TABLE 5.—FAT IN CORN PLANTED AND HARVESTED ON HIGH-FAT PLOT IN 1898.

Plot row No.	Corn planted.		Corn harvested.	
	Corn No.	Fat. Per cent.	Corn No.	Fat. Per cent.
1	521	4.98	1240	4.86
2	533	4.98	1250	4.74
3	486	5.03	1260	4.94
4	531	5.04	1270	5.17
5	568	5.05	1280	5.36
6	528	5.12	1290	4.79
7	546	5.20	1300	4.87
8	534	5.27	1310	5.20
9	478	5.39	1320	5.16
10	511	5.44	1330	5.25
11	501	5.45	1240	5.21
12	524	5.68	1350	5.63
13	513	5.49	1360	5.21
14	512	5.45	1370	5.44
15	527	5.43	1380	5.48
16	514	5.39	1390	5.26
17	517	5.26	1400	5.55
18	559	5.12	1410	5.23
19	484	5.07	1420	5.06
20	544	5.02	1430	4.89
21	508	5.04	1440	5.00
22	547	5.00	1450	5.10
23	536	4.97	1460	5.05
24	494	4.97	1470	5.21
Plot averages,		5.20	5.15	

TABLE 6.—FAT IN CORN PLANTED AND HARVESTED ON LOW-FAT PLOT IN 1898.

Plot row No.	Corn planted.		Corn harvested.	
	Corn No.	Fat. Per cent.	Corn No.	Fat. Per cent.
1	589	3.85	1480	3.97
2	574	3.83	1490	4.32
3	592	3.72	1500	4.08
4	602	3.55	1510	3.99
5	594	3.39	1520	3.81
6	614	3.39	1530	3.81
7	593	3.38	1540	3.69
8	606	3.50	1550	3.78
9	588	3.70	1560	3.93
10	603	3.80	1570	4.18
11	611	3.84	1580	4.21
12	591	3.85	1590	4.11
Plot averages,		3.65	3.99	

The average fat content of the corn from the high-fat plot for 1898 is 5.15 per cent., while 3.99 is the average percentage of fat in the corn from the low-fat plot, making a difference of 1.16 per cent. between the averages. The difference becomes 1.45 per cent. if we consider only the central half of each plot, or 1.56 per cent. if only the central third of each plot is considered. Even the effect of planting the seed in gradation as to fat content from the center rows to either side is decidedly noticeable in the crop. It is only necessary to take averages of the fat content of the composite samples from the high-fat plot in groups of four to obtain a regular gradation in the same order as that of the seed. Thus:

Corn. From rows.	Fat. Average per cent.
1-4	4.93
5-8	5.06
9-12	5.31
13-16	5.35
17-20	5.18
21-24	5.09

In the low-fat plot the percentages of fat in the composite samples *from the single rows* are in regular gradation, if we omit only the outside rows, Nos. 1 and 12. This may be seen in Table 6.

In 1898 a third plot of ground for the study of the fat content of corn was planted. This is called the "mixed-fat plot," and was planted after the same plan as the mixed-protein plot. In each hill two kernels of high-fat corn were planted on one side and two of low-fat content on the other. The special object in this work was, of course, to avoid the influence of soil differences. From this mixed-fat plot twenty-seven pairs of ears were taken from twenty-seven hills, one ear in each pair having been grown from high-fat seed and the other ear from low-fat seed. Table 7 gives the fat content in the corn from each of these ears.

TABLE 7.—FAT IN CORN FROM FIFTY-FOUR EARS GROWN ON THE MIXED-FAT PLOT IN 1898.

Hill No.	From high-fat seed.		From low-fat seed.	
	Corn No.	Fat. Per cent.	Corn No.	Fat. Per cent.
1	762	4.05	761	3.82
2	764	4.42	763	3.62
3	766	4.65	765	3.03
4	768	4.90	767	3.92
5	770	5.16	769	3.94
6	772	5.06	771	3.99
7	774	5.13	773	4.15
8	776	4.95	775	3.75
9	778	5.59	777	3.60
10	780	4.10	779	4.04
11	782	4.49	781	3.56
12	784	5.25	783	4.26
13	786	5.65	785	4.15
14	788	5.03	787	4.08
15	790	5.57	789	3.57
16	792	5.32	791	4.69
17	794	5.75	793	3.96
18	796	4.95	795	4.64
19	798	4.79	797	4.30
20	800	4.59	799	4.33
21	802	5.56	801	3.77
22	804	5.34	803	4.17
23	806	4.92	805	4.50
24	808	5.91	807	3.58
25	810	5.86	809	4.55
26	812	4.59	811	3.96
27	814	5.02	813	4.23
Averages,		5.06	4.01	

The average percentage of fat in the twenty-seven ears from the high-fat seed is 5.06, while 4.01 per cent. is the average fat content of the twenty-seven ears from the low-fat seed. It is interesting to note that in the twenty-seven hills there is no instance where the ear of corn from high-fat seed does not contain more fat than the ear grown from low-fat seed in the same hill.

The ear which grew from low-fat seed in hill No. 3 has the lowest fat content, 3.03 per cent., of any ear of corn which has been analyzed in these experiments. The maximum fat con-



Fig. 2.

tent which has been found in an ear of Burr's White corn up to the present time is 6.71 per cent.

The fact that the fat, or oil, of the corn kernel is contained almost entirely in the germ¹ suggested to the writer the possibility of selecting corn of either high- or low-fat content by mechanical examination of the kernel and judging as to the quantity of germ compared with the remainder of the kernel. It was found that the method is possible and rather more satisfactory than the method (already described) of judging the protein content of the corn kernel by mechanical examination, as it is less complicated than the latter.

Figure 2 (made from a photograph taken with a magnification of three diameters) illustrates the difference in corn kernels of about the same size but a very different fat content. The cross sections shown at the top were made by cutting off about one-fifth of the kernel from the tip end. In the longitudinal sections the tip end of the kernel points downward to the left. The sections and whole kernel shown at the left are from an ear of corn which contains 6.08 per cent. of fat. Those at the right are from an ear containing 3.64 per cent. of fat. It will be seen that the germ is larger in the high-fat corn and that it extends nearly the entire length of the kernel, while in the low-fat corn the germ is small and only about two-thirds as long as the kernel.

To obtain exact data as to the relation between the percentage of fat and the percentage of germ in the corn kernel, the germs were removed² from a large number of kernels, the weight of the whole kernel and also of the separated germ being determined, and reported on the basis of dry matter, having been dried in hydrogen before being weighed. Table 8 will serve to illustrate the results obtained in this work.

¹ See University of Illinois Agricultural Experiment Station, Bulletin 53, 139, 140 (1898).

² It was found that after soaking corn kernels in hot water for about thirty minutes the germs are easily removed in the entire state and quite free from other portions of the kernel.

TABLE 8.—WEIGHT OF CORN KERNELS WITH WEIGHT AND PERCENTAGE OF GERMS.

Corn No. 1352—Fat = 6.71 per cent.				Corn No. 1529—Fat = 3.22 per cent.			
Kernel No.	Kernel weight. Gram.	Germ weight. Gram.	Germ. Per cent.	Kernel No.	Kernel weight. Gram.	Germ weight. Gram.	Germ. Per cent.
1	0.3113	0.0391	12.56	1	0.2859	0.0250	8.74
2	0.2872	0.0360	12.53	2	0.2882	0.0237	8.22
3	0.2864	0.0340	11.87	3	0.3533	0.0297	8.41
4	0.2821	0.0374	13.26	4	0.3135	0.0265	8.45
5	0.2667	0.0360	13.50	5	0.3277	0.0273	8.33
6	0.3694	0.0442	11.97	6	0.3417	0.0310	9.07
7	0.3434	0.0414	12.06	7	0.2918	0.0257	8.81
8	0.2682	0.0300	11.18	8	0.3178	0.0276	8.68
9	0.3116	0.0402	12.90	9	0.3273	0.0278	8.49
10	0.2870	0.0348	12.13	10	0.3338	0.0280	8.39
Av'ges,	0.3013	0.0373	12.40	Averages,	0.3181	0.0272	8.56

In corn No. 1352, containing 6.71 per cent. of fat, and corn No. 1529, containing 3.22 per cent. of fat, the kernels are approximately uniform in size, the former being 0.3013 and the latter 0.3181 gram in average weight; but the germs in the high-fat ear amount to 12.40 per cent. of the whole kernels, and to only 8.56 per cent. in the low-fat ear. This difference in percentage is due to the absolute difference in the size of the germs, the germs from the high-fat kernels being 0.0373 gram and from the low-fat kernels only 0.0272 gram average weight.

From a large amount of data the general relation between the percentage of fat and the percentage of germ in the corn kernel has been clearly established. Of course there are minor individual differences among the kernels from the same ear, and it has also been noted that there is a difference in different ears as to the relation between fat content and germ content. These minor differences are perhaps due in part to the varying percentage of fat in the body of the kernel, but the variation in the percentage of fat in the germs, especially from different ears, is doubtless the chief factor in producing such differences. For example, Voorhees¹ found 26.65 per cent. of fat in the germs of the corn kernel, while Balland² found 39.85 per cent.

The method of selecting corn of high- or low-fat content by mechanical examination is similar to that described under the work on the protein content of corn, excepting that the size of

¹ New Jersey Agricultural Experiment Station, Bulletin 105 (1894).

² *Compt. rend.*, 122, 1004 (1896).

the germ alone as compared with the remainder of the kernel is considered. Judgment is formed by examining with the naked eye the cross sections and longitudinal sections of a few kernels from each ear. To make a practical test of the method nearly 300 ears of corn were examined, which varied in fat content¹ from about 3.60 to 5.80 per cent. From this lot of corn, by mechanical examination, eighteen ears were selected which appeared to possess a comparatively high-fat content, and at the same time thirty ears apparently low in fat were picked out. Tables 9 and 10 show the results in detail, the percentage of fat in the corn from each ear being given as previously determined by chemical analysis.

TABLE 9.—FAT CONTENT OF EIGHTEEN EARS SELECTED BY MECHANICAL EXAMINATION FOR HIGH-FAT CORN.

Ear No.	Fat. Per cent.	Ear No.	Fat. Per cent.
1	4.94	10	5.33
2	4.30	11	5.55
3	5.43	12	4.99
4	5.64	13	5.27
5	5.23	14	5.12
6	5.58	15	5.73
7	5.06	16	5.43
8	5.26	17	4.97
9	5.22	18	5.21

Average, 5.24

TABLE 10.—FAT CONTENT OF THIRTY EARS SELECTED BY MECHANICAL EXAMINATION FOR LOW-FAT CORN.

Ear No.	Fat. Per cent.	Ear No.	Fat. Per cent.
1	4.01	16	3.63
2	4.11	17	4.02
3	3.64	18	4.55
4	3.67	19	4.52
5	4.52	20	4.29
6	3.66	21	3.81
7	4.07	22	4.39
8	4.20	23	4.43
9	3.91	24	3.80
10	4.85	25	4.09
11	4.35	26	4.27
12	4.52	27	4.02
13	3.73	28	3.87
14	3.76	29	4.00
15	5.21	30	3.98

Average, 4.13

¹ Twelve ears of corn of very high fat content and sixteen ears of very low fat content had been previously taken from this lot and used for seed in 1899, otherwise the results would no doubt have been even more marked than they are.

The average fat content of the ears selected for high-fat corn is 5.24 per cent., while 4.13 is the average of that selected for low-fat corn. If we omit a single ear from each set, the lowest percentage of fat in the ears selected for high-fat content is higher than the highest percentage of fat in the low-fat selection.

SUMMARY AND DEDUCTIONS.

All results thus far obtained from our experiments indicate that it is not only possible but entirely practicable to influence the chemical composition of corn, that by proper selection of seed any of its principal constituents, protein, fat, or carbohydrates, may be increased or decreased.

In every experiment the selection of seed corn of high- and of low-protein content has produced marked effects in the crop, differences varying from 0.50 to 1.25 per cent. of protein; and in the experiments to influence the fat content of corn, the selection of seed of high- and of low-fat content has produced differences in the crops varying from 0.67 to 1.45 per cent. of fat.

Considering the fact that the average fat content of Burr's White corn is less than five per cent., the proportion of fat in corn is much more susceptible to the influence of seed selection than is the protein content. This is doubtless due to the fact that the primary materials from which fat is manufactured, namely, carbon dioxide and water, are usually furnished to the plant in unlimited supply, while the formation of protein is essentially dependent upon the supply of available nitrogen in the soil.

As the percentage of carbohydrates (principally starch in corn) varies inversely with the combined percentages of protein and fat (neglecting the small percentage of ash found in corn), it follows that the carbohydrates are increased in percentage whenever the combined percentage of protein and fat is decreased, and *vice versa*.

By actual trial it has been found both possible and practicable to select corn by mechanical examination with either high or low content of protein, fat, or starch.

While further investigations are necessary and are in progress to determine more accurately the best methods and more definitely the possibilities of improvement in the chemical composition of corn, it is here stated, tentatively, that essentially by the

methods reported in this paper any corn-grower will be able to select seed and to breed corn to increase or to decrease the percentage of any of its three principal chemical constituents.

All experiments reported in this paper have been carried on with the one variety of corn, namely, Burr's White. Of course it is not believed that Burr's White is the very best variety for improvement in corn in every one of the several important lines. Indeed, it seems highly probable that one variety of corn will be found best adapted to but one line of improvement. We have in progress chemical studies of other varieties of corn, and a considerable amount of data and information has been already acquired, but it is reserved, pending further investigations for future publication, the special object of this article being to give some of the data, thus far obtained, indicating the possibility and establishing the fact that the corn kernel may be improved in chemical composition.

It may be stated that improvement in the composition of other parts of the corn plant is under consideration by the Illinois Station. Plans are also made to investigate other questions relating to this general subject; such as the effect of changes in the chemical composition of corn upon its digestibility, vitality, yield, etc.

The results obtained in our investigations to improve the composition of corn have suggested the possibility of improving other grains by somewhat similar methods. It seems not improbable that the different grains, or kernels, produced in a single head of wheat, oats, or barley, may be found to be approximately uniform in composition.¹ If so, a method is thus afforded for selecting seed and breeding those cereals upon the basis of the chemical composition of the grain.

UNIVERSITY OF ILLINOIS
AGRICULTURAL EXPERIMENT STATION.

NOTE.

The Determination of Chromium in Steel.—A method for the determination of chromium in steel, based upon its oxidation to chromic acid by potassium chlorate in nitric acid, and the titration of the chromic acid with ferrous sulphate and potassium

¹ Since this was written a chemical study of wheat has been begun in this laboratory, and in general the results thus far obtained support the suggestion which is offered above.

permanganate in the greatly diluted solution, has been described by McKenna.¹ I have found it accurate and rapid. Sargent and Faust² suggest sand held in place by a little glass-wool, and covered by a very thin layer of asbestos, for filtering the nitric acid solution, in order to remove the oxides of manganese. I have found paper a suitable filtering medium for the removal of these oxides. Another change in details which I am accustomed to employ, is the use of nitric acid and potassium chlorate in greatly reduced quantities.

Dissolve three grams of the sample in fifty cc. of concentrated hydrochloric acid, in a 400 cc. lipped beaker, covering with a (five inch) watch-glass. Boil down until little more than a moist cake is left. Add fifty cc. of concentrated nitric acid, and boil for a few minutes when the copious evolution of nitrous fumes will have largely ceased. Remove from the light, and when somewhat cooled, add four grams of potassium chlorate, and resume the boiling, continuing until the solution is reduced in volume to from twenty-five to thirty cc. Dilute to 300 cc. with cold water, and add fifteen cc. of ammonia of 0.90 sp. gr. Mix thoroughly by stirring and filter the solution (first cooled if necessary) through a ribbed double paper, washing with cold water. Dilute the filtrate and washings to about 450 cc., and titrate with standard solutions of ferrous ammonium sulphate, and potassium permanganate. The best, that is the most accurate and simplest, way of standardizing these solutions is by means of a standard solution of potassium bichromate.

I have made some hundreds of experiments upon the amounts of reagents needed for the successful execution of this estimation, the extent to which the concentration by boiling must be carried, and the amount allowable of free nitric acid in the solution, before filtration through paper.

When three grams of steel are used for an estimation, from one to two grams of potassium chlorate are taken in many cases, and sometimes one-half gram, is sufficient to oxidize the chromium, if perfect removal of hydrochloric acid by nitric was first effected. The last traces of hydrochloric acid are, however, more conveniently removed by potassium chlorate.

It is evident that a solution of chromic acid if brought into

¹ Proceedings of Engineers' Society of Western Pennsylvania, 11, No. 6.

² This Journal, 21, 287.

contact with a paper filter, should be dilute and cold to avoid reduction. It is necessary also that not too much free nitric acid be present. The conditions for avoiding reduction by paper, are shown by the following results: They were obtained by titration of twenty cc. of potassium bichromate solution, which contained a quantity of chromium equal to 1.03 per cent. in three grams of steel. Each test was conducted as follows: the bichromate, nitric acid, and water were brought to the temperature desired, this being either nearly boiling, or cold to the touch, two washed papers placed in the beaker, and the whole stirred for five minutes, filtered through a ribbed paper, and the filtrate titrated after dilution to 450 cc.

Number of the experiment.	Nitric acid (1.42 sp. gr.) added before filtration. cc.	Temperature.	Volume filtered. cc.	Chromium expressed as a percentage for three grams of steel.	Remarks.
1....	0	1.03	No paper placed in this; no filtration.
2....	20	1.03	" " " " " " "
3....	5	cold	300	1.03	
4....	5	"	300	3.08	Sixty cc. of bichromate solution used.
5....	5	"	100	1.02	
6....	5	hot	100	0.95	
7....	10	cold	300	1.00	
8....	20	"	300	0.97	
9....	20	"	300	1.00	No paper placed in this; simply filtered.
10....	20	hot	300	0.96	" " " " " " "
11....	20	"	100	0.86	" " " " " " "

FOUR DETERMINATIONS OF CHROMIUM IN A CHROME STEEL.

Percentage of chromium.

0.80 Filtered through asbestos.

0.81 " " "

0.81 } Method described; filtering through paper.

0.81

RESULTS FROM ANALYZING SOLUTIONS OF KNOWN CONTENTS IN CHROMIUM.

These solutions were prepared as follows: three grams of steel containing no chromium were dissolved in hydrochloric acid, and a measured quantity of a standard solution of potas-

¹ Accuracy.

sium bichromate, reduced to chromic chloride by hydrochloric acid and alcohol, added.

These solutions were boiled down until little more than a moist cake was left, and the analysis in each case, further conducted exactly as described in the modified method, above given.

PERCENTAGE OF CHROMIUM.

True.	Found.
1.55	1.54
1.55	1.52
1.03	1.04
1.03	1.04
3.09	3.11

Addendum—Gravimetric Determination of Manganese in Steel.

—The manganese precipitate collected upon a paper filter is a convenient starting-point for its gravimetric estimation. The solution of the precipitate in hydrochloric acid is to be treated in the customary way, the trace of iron being precipitated as basic acetate, and the manganese as manganous ammonium phosphate in the filtrate therefrom.

R. W. MAHON.

NEW BOOKS.

THE DISCHARGE OF ELECTRICITY THROUGH GASES. BY J. J. THOMSON, Professor in the University of Cambridge. New York: Charles Scribner's Sons. 1898. 203 pp.

This work of Prof. Thomson's represents the material of lectures delivered by him in October, 1896, at the sesquicentennial celebration of Princeton University, but amplified with a record of later observations. As the subject is one of comparatively recent date, it is hardly to be expected that the ground should have been so uniformly covered as to enable the writer to give a thoroughly connected account of the peculiar phenomena, that he and others have observed, in the fashion of a text-book. On the other hand, the fact that the essays were to be delivered orally precluded a purely historical presentation of discoveries, with a detailed account of the author's own work upon the subject. In place of these, we have a very lucid and fair exposition of the most striking facts, and an impartial statement of the most noteworthy hypotheses involved. The book is therefore chiefly useful as a guide through the intricate meshwork of hypotheses, which recent years have produced.

The difficulties of the subject seem to result largely from the impediments which interfere with the immediate observation of electrical phenomena in gases. In almost every case, the aid of solids or liquids must be called in, to convey the phenomenon to the observer, and the question often arises as to whether such phenomenon is not produced upon the surface of such liquid or solid.

The first chapter is devoted to the methods that can be employed for conveying an electric charge to a gas,—no easy task, according to the authors: liberation of the gas from a liquid undergoing electrolysis, the splashing of liquids through the gas, and the Röntgen rays, are resorted to. The second chapter, entitled photoelectric effects, really embodies the little that is known about the electric conductivity of gases, and its variation under the influence of different forms of radiant energy. Thomson apparently ascribes gaseous conduction to electrolysis, either in the purely chemical sense of the decomposition into ions, or in that of the association or dissociation of molecular complexes. A rather short chapter on the cathode rays has apparently been added as an extension of this hypothesis to the explanation of the results obtained by Lenard, Röntgen, and so many others. Contrary to the views of most of these physicists, Thomson ascribes the phenomena outside the vacuum tube to motions of gaseous matter, rather than of the "ether." As carriers of the rays, he looks for small particles, traveling at a high rate of speed and encountering fewer obstacles than would molecules or atoms. He assumes that atoms in fact consist of particles bearing the same relation to the total atom that the molecule does to the ordinary gas volume. Lockyer imagined that such particles were torn asunder by the heat of the solar atmosphere. Thomson thinks it likely that some higher order of electrolysis shatters the atoms that impinge upon the highly electrified cathode.

This, and other suggestive matter, is set forth in clear language and attractive style. The book is well printed and finely illustrated.

MORRIS LOEB.

EASY EXPERIMENTS OF ORGANIC CHEMISTRY. BY JOHN HOWARD APPLETON. Providence, R. I.: Snow and Farnham. 1898. 107 pp. Price, 60 cents.

There seems to be a general agreement in the study of

chemistry that, while the text-book work should be explained and illustrated by lectures, it should also be supplemented by laboratory work on the part of the student. Several excellent text-books on organic chemistry are now to be found in which a considerable number of illustrative experiments are described, but they are arranged to be performed either by the lecturer or by the student or by both, and in the attempt to satisfy two conditions they fail to meet either to the best advantage.

The book under consideration is intended solely for the student and for use in the laboratory, and it is characterized by a marked simplicity, directness and clearness of style, and by the very simple character of the apparatus and the very moderate amounts of materials to be employed, conditions which enable the untrained observer the more readily to observe the phenomena that occur, and to distinguish the essential from the non-essential.

No doubt, with such a fund of experiments to draw upon, as is now at the command of chemists, each person who sets out to arrange a course of experiments would prepare one that differed in some particulars from this, but Professor Appleton has selected fairly typical and instructive examples which can be performed in an easy and rapid manner, and he has arranged them in the order in which the topics are usually treated in text-books on organic chemistry so that the book can be used in connection with any introductory course, and it will be found to be a safe one to put into the hands of a student. A very commendable feature of the book is the "cautions" that are appended to the description of each experiment which is attended with any danger in its performance, for the author has thus relieved the teacher, in these instances, of a very grave duty.

CHARLES E. MUNROE.

A SELECT BIBLIOGRAPHY OF CHEMISTRY, 1492-1897. BY H. CARRINGTON BOLTON. First Supplement. City of Washington: Published by the Smithsonian Institution. 1899. Large 8vo. ix + 489 pp..

This first supplement contains 5,554 titles in addition to the 12,031 contained in the volume issued in 1893. Of these, 2,050 titles were contributed by others. Many of the titles have, of course, been added by the author in bringing the book down to the close of 1897, but a considerable number have probably been

added which he had previously overlooked. To most chemists the task which Dr. Bolton has completed would seem an appalling one. To those who know him personally his success will not seem surprising. It is a wonderful book in every respect. Dr. Bolton's interest in this matter is further evidenced by his recent letter to *Science*, printed also in the *Chemical News*, of July 7.

E. H.

SCHOOL CHEMISTRY. BY CHARLES BASKERVILLE, PH.D., The University of North Carolina. Richmond, Va.: B. F. Johnson Publishing Co. 1899. 159 pp. Price, 60 cents.

This book has been prepared for use in high schools, and academies, and is intended to give the pupil an elementary knowledge of the more important chemical facts and theories, especially those connected with every-day life. The book is divided into thirty-seven lessons, each of which consists of a few pages of descriptive text, followed by several well-described and pertinent experiments. Water is first taken up, then atoms, oxygen, air, oxidation, the other non-metals, five lessons on organic chemistry, metals, salts, the soil, vegetable and animal chemistry. The aim of the book is well carried out by the author, but it may be questioned whether the aim of "school" chemistry should not be primarily to train and discipline the mind by the use of the scientific method, as well as to interest the pupil in the study of natural science, and only secondarily to impart knowledge of chemical facts and theory. This order is reversed by the author.

The make-up of the book is good, the proof-reading unusually thorough, but the book is marred by many carelessly constructed sentences and loose statements. There is a very complete index.

JAS. LEWIS HOWE.

A SHORT HISTORY OF THE PROGRESS OF SCIENTIFIC CHEMISTRY IN OUR OWN TIMES. BY WILLIAM A. TILDEN. Longmans, Green, and Co., 39 Paternoster Row, London, New York, and Bombay. 1899. ix+276 pp. 12mo.

Dr. Tilden, the well-known professor of chemistry in the Royal College of Science, London, in the spring of 1898, gave a course of lectures to working-men on the progress made in the science and practice of chemistry during the preceding sixty years. Only able to sketch in very broad outline the general features of the subject, he felt the need of some book of moderate size to

which he could refer his hearers, and which would afford a historical survey of the succession of events that led up to the system of theory in chemistry accepted at the present day. Finding no such book he wrote the volume under review. To appreciate the work one must have some knowledge of elementary physics and chemistry, for it does not profess to be a text-book. The period covered by Dr. Tilden, corresponds to the reign of Queen Victoria, and the book might well have been named "Evolution of Chemistry in the Victorian Era." In ten chapters, the author treats of matter and energy; the distribution of the chemical elements and their recognition by the chemist; the rectification and standardization of atomic weights; the numerical relations among the atomic weights and classification of the elements; origin and development of the ideas of valency, and the linking of atoms; the development of synthetical chemistry; the origin of stereochemistry; electricity and chemical affinity; and the liquefaction of gases.

Dr. Tilden writes clearly, has a full acquaintance with his subject, and selects the material judiciously; he is liberal in giving credit to each discoverer for his share of joint work in developing a given theory or law. In writing of the development of certain branches of chemistry he recognizes the work of our own Morley, J. P. Cooke, and F. W. Clarke, as well as that of the French, Russians, Germans, and Italians.

At the close of the volume the author gives a useful list of "Important Events Arranged in Chronological Order;" in this we find the invention of Bunsen's gas-burner credited to the year 1866, but the reviewer is perfectly certain that the "Bunsen-burner" was used in the Heidelberg laboratory many years earlier; it was thought no novelty in 1864.

Dr. Tilden writes in conclusion:

"In the ancient universities of Great Britain . . . the spirit of mediævalism is no longer wholly predominant. We may therefore look forward hopefully to the day, not far distant, when science and letters, no longer fierce competitors for academic vintage, may walk hand in hand, each conscious of her own dignity, but ready to yield to the other her due share of honor."

The volume successfully carries out the intentions of the

author, and can be recommended to all interested in the development of physical science. HENRY CARRINGTON BOLTON.

EXAMINATION OF WATER CHEMICAL AND BACTERIOLOGICAL. BY WILLIAM P. MASON. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1899. 135 pp. Illustrated. Price, \$1.25.

This book is divided into three parts: First, an introduction, pointing out the popular misconception of water analysis and emphasizing the necessity of knowing the source of the sample in order to properly interpret the result of the analysis. To this end, throughout the book, much matter is given to enable the analyst to pass upon the quality of a drinking-water from his analysis. Part two gives directions for sampling, and methods of chemical analysis. It is needless to say that these latter, coming from such an authority upon water analysis, as Prof. Mason, are of the best, and are well arranged. Part three deals with so much of the biological examination of water as is of most use to the chemist, leaving the wider field of ultimate differentiation to the biologist.

RICHARD K. MEADE.

THE LIQUEFACTION OF GASES. BY J. CAURO. Paris: Gauthier-Villars. 1899. 83 pp.

This treatise on the liquefaction of gases has the thoroughness that one might expect if it were prepared for presentation to a class of students specializing in the subject. There is a cryogenic laboratory at Leyden; it is not hard to foresee the establishment of a chair of *cryogenics* at some enterprising university. But everyone at the present moment wants the thermodynamics of gases explained to him. It should be done scientifically, fully, and consecutively. The mathematics involved is anything but abstruse; the facts are entertaining and the story of the successive steps in its history positively fascinating. The work in review could hardly be more fitted to serve for such a purpose as a full scientific presentation of the subject.

The discussion of the physics of gases in the first chapter, of their curves near the critical-point and of isothermals, leads up to the discussion of the Joule-Thomson effect, and closes with a scheme of methods of refrigeration. It is interesting to note amongst these "the principle of cascades." This was the basis of Pictet's work. Another way of expressing it would be by successive falls in the critical-points of the liquids used, one being volatilized to chill the next, and so on until the required

temperature is reached, when a low pressure will be effective for the liquefaction required. Also, the much-discussed application of the Joule-Thomson effect or gain in the circulatory, self-cooling, expansion or sudden-release methods.

In the description of the experimental work of the past, and the practical methods of liquefaction now in use, all the workers in the field seem to have received their just meed of notice, and no signs of dispute about priority are given. A chapter is taken up with historical data, mention of papers, their dates of publication, etc., and the last entry records the communication of Dewar, to the Royal Society, May 10, 1898, reporting the production of liquid hydrogen and helium. In the last chapter are given the applications of liquefied gases, and certain ideas suggestive for chemists are found here such as the preparation of pure oxygen from liquid air, the possible use of liquefaction for separation or analysis of gases, for concentration of solutions, preparation of salts, etc. No thermometric or cryometric methods are mentioned except the mere reference to the use of a hydrogen thermometer by Olzewski. It is a curious sin of omission, as this is now a most promising field of physical research and pertinent to the author's subject. C. F. MCKENNA.

ELEMENTARY STUDIES IN CHEMISTRY. BY JOSEPH TORREY, JR., Instructor in Harvard Univ. New York: Henry Holt & Co. 12mo. 49 illustrations. viii + 487 pp.

Some years ago during a symposium on the teaching of chemistry Dr. F. W. Clarke remarked that the best method to be pursued depended altogether upon circumstances,—upon the age of the pupils, their previous training, etc. The statement contained a great deal of practical wisdom. Few teachers fail to be profoundly influenced by their environment. If they write textbooks for student use as Professor Torrey has done the nature of this environment becomes at once more or less evident. Professor Torrey has charge of the chemical instruction in the Summer School of Harvard University, and in preparing this book he has evidently had in mind the needs of the class of students who attend such schools—mainly teachers, with inadequate training, bent on self-improvement, willing and anxious to work, mature in years and experience.

The book bears ample evidence of great care in preparation. It is not too much to say of it that it contains one of the most carefully constructed and logical arguments from chemical fact to chemical theory that has ever been written.

In plan the idea is comprehensive. It is to teach the elements of all phases of chemical science. Nothing is shirked, and every point is clearly and sufficiently explained. Each day's work consists of two parts: Laboratory work which comes first and establishes the facts, and the lecture which follows, explains, systematizes, and enlarges on them. While the sequence of treatment is largely in accordance with the periodic law the author by no means binds himself to this order, considering the needs of the student of first importance.

The book contains a few slips in statement of facts, fortunately of small importance, and some infelicities of expression. These will doubtless be remedied in subsequent editions. Every teacher can learn something from Professor Torrey, and all should read his book.

E. H.

THE MINERAL INDUSTRY: ITS STATISTICS, TECHNOLOGY AND TRADE IN THE UNITED STATES AND OTHER COUNTRIES TO THE END OF 1898.
EDITED BY R. P. ROTHWELL. VOLUME VII. New York and London:
The Scientific Publishing Co. 1899. 4to. xxviii+982 pp. Price, \$5.00.

To the chemist and technologist the annual volumes of this series are of great interest and value, embodying as they do the latest progress in the different departments of metallurgy and mining. Much of the information is original and cannot be found elsewhere. Among the items of interest contained, it may be noted that the production of aluminum in the United States was 5,200,000 pounds. Ferromolybdenum was produced to the extent of 2,100 pounds, valued nominally at 50 cents per pound. Molybdenum was first produced in the United States to the amount of 9,550 pounds, worth about \$1.25 per pound. 33,200 pounds of metallic tungsten, 1,594,152 pounds of carborundum, 3,584,586 barrels of Portland cement of 400 pounds each, 185,647 pounds of artificial graphite, and 8 tons of molybdenite were produced in this year.

The volume contains a vast amount of information, of which it is impossible to give even a digest in the space available. There are articles, for instance, upon the manufacture of con-

centrated alum, asphaltum refining, the hydraulic cement industry, firebrick manufacture, kaolin, the electrolysis and refining of copper, the identification of gems, the technology of gypsum, lime and lime-burning, manufacture of acid phosphate of lime, occurrence and recovery of sodium carbonate in the great basin, manufacture of chamber sulphuric acid, and numerous articles on progress in metallurgy written by specialists.

E. H.

THE RISE AND DEVELOPMENT OF THE LIQUEFACTION OF GASES. BY WILLETT L. HARDIN, Ph.D. New York and London: The Macmillan Company. 1899. 244 pp. Price, \$1.50.

The recent achievements in the liquefaction of gases, and the very general interest which of late has been manifested in this line of investigation has naturally led to the publication of several works on this subject. One of the best of these is the volume by Dr. Hardin. In the preface the author states that "while the book has been written in a popular-science style, an effort has been made to make it of value to those who are especially interested in the subject by giving the references to the original literature." This latter feature might be adopted with great advantage in all books of a similar nature.

The author devotes about one-third of the volume to an account of the results obtained by the earlier experiments up to about 1860, including the work of Faraday, Thilorier, Natterer, and others. Then follows a chapter on critical constants, the continuity of the gaseous and liquid states of matter, and a statement of the equation of Van der Waals.

The second half of the book is devoted to the liquefaction of the so-called permanent gases, commencing with the methods employed and the results obtained by Cailletet and by Pictet in 1877. A section is devoted to the experiments of Wroblewski and Olszewski, and those of Dewar. Several pages are given to the so-called regenerative method which has been employed by Linde and by Tripler in the liquefaction of air on a large scale. Another section is devoted to the liquefaction of argon and helium, and to the method employed by Dewar in the production of liquid hydrogen in a static condition. A table of physical constants is given, and in conclusion the author discusses briefly the three states of matter, some of the applications of liquefied

gases, and the effect of low temperatures upon physiological action. The volume is a clear, well considered, and reasonably full statement of our present knowledge on the liquefaction of gases.

E. G. LOVE.

QUALITATIVE ANALYSIS FOR SECONDARY SCHOOLS. BY CYRUS W. IRISH, A.B. New York: American Book Company. 100 pp.

The usual college course in qualitative analysis is simplified by omitting oxalates and phosphates, and determinations other than spectroscopic for sodium and potassium. The test for chromium is made more striking by oxidation with hydrogen dioxide and subsequent precipitation as lead chromate; the alternative method by fusion is also given. Preliminary experiments on bases are the customary ones, all bearing directly on qualitative separations, but they hardly carry out the author's prefatory claim of a study of descriptive chemistry of bases by laboratory methods. A praiseworthy effort is made to keep alive the student's interest in general descriptive chemistry by a considerable number of questions on that subject. Questions are put also on the experiments performed. Uniformly these call into play only the student's power of observation, and it would seem well to ask some questions beginning with "why"; questions to bring out reasons for steps taken. Observations of the form of precipitate, whether flocculent, crystalline, etc., are omitted. Likewise omitted, are directions for careful manipulation. An unsatisfactory condition of mind and knowledge must result from this statement regarding the solubility of freshly precipitated zinc sulphide in hydrochloric acid: "To confirm the presence of Zn add conc. HCl, when ZnS, if present, will be dissolved, but S in suspension will not dissolve. A partial solution, on addition of conc. HCl, also indicates ZnS." This should be a satisfactory manual in the hands of a good teacher. It will not compel good teaching.

H. M. ULLMANN.

THE ELEMENTS OF BLOWPIPE ANALYSIS. BY FREDERICK HUTTON GETMAN, F.C.S. New York: The Macmillan Company. 1899. Small 12mo. 77 pp. Price, 60 cents.

The book begins with cuts of blowpipe apparatus, poorly executed, some important ones omitted, while that of the blowpipe itself shows an antiquated form very seldom used.

Chapter I describes in a fragmentary manner the common apparatus and reagents, omitting some of the most useful. The recommendation to use for blowpiping a Buhsen flame one centimeter high with air supply cut off, is unfortunate. Half a dozen other devices are better.

Chapter II gives a general outline of blowpipe analysis, following the six primary tests of Berzelius. Here, several of the most valuable blowpipe tests, such as examination in an open glass tube, are omitted altogether. The tests given are only partially described, many details necessary for successful practice being omitted.

Chapter III, giving reactions for the detection of the elements, arranged alphabetically, is very unsatisfactory. The reactions given are, in general, those of the oxides only, and misstatements are numerous. Chapter IV, giving the behavior of some of the principal metallic ores, is little better.

There are in the book at least a score of downright misstatements, and another score which are inaccurate because of their incompleteness. The omissions are startling,—gold, selenium, tellurium, molybdenum, titanium, tungsten, uranium, and vanadium not being even mentioned in any connection.

What is correct in the book is well expressed, and the type is clear, but the book as a whole does not deserve a place in blowpipe literature.

JOSEPH W. RICHARDS.

A TREATISE ON THE KINETIC THEORY OF GASES. BY S. H. BURBURY, M.A., F.R.S. J. and C. F. Clay at the University Press, Cambridge. New York: The Macmillan Company. 1899. vii + 157 pp. Price, eight shillings.

The object of this book as expressed by the author is to apply to the kinetic theory of gases a method of analysis different from that generally employed. Previous writers have always started with the fundamental assumption that with regard to their relative motion the molecules of a gas are independent of one another. To express this independence the law of distribution of momenta assumes the form $E^{-\lambda Q}$, and the expression relating to the translation velocities becomes, $Q = \sum m(u^2 + v^2 + w^2)$, m being the mass and u , v , and w the component velocities. Boltzmann deduces his H theorem and the theorem of the equality of

mean kinetic energy for each degree of freedom from the above-mentioned independence and from the form of Q given. The author gives to Q the form $Q = \sum m(u^2 + v^2 + w^2) + \sum \sum b(uu' + vv' + ww')$, where b is a negative function of the distance r at the instant considered between the two molecules whose velocities are u, u' , etc., which function is inappreciable except for very small values of r . The author shows that without the coefficient b the motion can not be stationary. Other investigators have proved that assuming the independence, the motion is stationary; the author does not question the proof but the axiom. The result of giving to Q the new value is that molecules near to each other have on an average a motion in the same direction; *i. e.*, they tend to form streams. The author admits that the usual form holds very well for ordinary gases under ordinary conditions, since for them the b coefficients are probably very small, but he maintains that his form is more general, applying without restriction as to density, except when the gas is liquefied or very near its point of liquefaction.

The subject is treated in ten chapters to which is added a short appendix containing proofs of certain mathematical propositions (relating chiefly to determinants) used in the book. Throughout the work the author considers critically the methods and results of other prominent writers on the kinetic theory in connection with his own. The style is clear and forcible. The book is not a treatise that seeks to present the subject in an elementary form; it is rather a piece of original work which every student of the kinetic theory should read.

The book is printed on good paper. The type is clear and the cloth binding is neat and durable.

The appearance of this book is additional evidence that interest in the kinetic theory is still being maintained in spite of the fact that kinetic explanations are at present viewed rather with disfavor by a number of prominent scientists.

LOUIS KAHLENBERG.

INORGANIC CHEMICAL PREPARATIONS. BY FELIX LENGFELD, Assistant Professor of Inorganic Chemistry in the University of Chicago. The Macmillan Company. 1899. 57 pp.

The teaching of inorganic chemistry in the laboratory has been developed along analytical lines almost entirely. While there is

getting to be a livelier appreciation of the value of the synthetical chemistry as a part of every chemist's training, there is even now a comparatively small number of laboratories where a regular course in the preparation of pure inorganic compounds from crude and impure materials, is required of the students. Wherever such a course is offered, or contemplated this little book of Dr. Lengfeld's will be welcomed. It contains careful and *workable* directions for the preparation of about fifty compounds, beginning with easily prepared substances, like sodium chloride, potassium chlorate, and acid sodium carbonate, and proceeding with compounds the preparation of which requires greater experience and skill, and finally ending with hydrogen dioxide, hydroxylamine sulphate, and phosphonium iodide.

To quote from the preface: "An attempt has been made to introduce all processes generally used, and at the same time to avoid repetition. The student should study each preparation in detail, work out other methods of making the same substance, understand and criticise every step he takes and read some original articles. Therefore references to the literature have been given." The student who conscientiously follows this advice, and works through such a list of preparations, will find his knowledge of chemistry increased quite as much as it would be by any equal amount of labor that he could undertake.

G. M. RICHARDSON.

THE ELEMENTS OF QUALITATIVE ANALYSIS. By WM. A. NOYES, PH.D., Professor of Chemistry in the Rose Polytechnic Institute. Fourth Edition. Henry Holt & Co. 1897. 97 pp. Price, 88 cents.

Each one of the earlier editions of this work has proved itself an extremely useful and complete outline of the general subject covered by Fresenius in his larger work on Qualitative Analysis. The present edition does not differ radically from those preceding it, but it embodies many useful additions and minor changes, which will increase its value. Its mode of treatment throughout is characterized by the same explicitness in the directions to students. Copious tables of reactions are a feature of the book. A brief introductory chapter upon the dissociation theory of solutions calls attention to the many applications of the theory

and emphasizes the importance which it seems likely to take in the near future in the teaching of analytical chemistry.

F. C. PHILLIPS.

THE COMPENDIOUS MANUAL OF QUALITATIVE CHEMICAL ANALYSIS OF C. W. ELIOT AND F. H. STORER, AS REVISED BY W. R. NICHOLS. By W. B. LINDSAY, Professor of General and Analytical Chemistry in Dickinson College, and F. H. STORER, Professor of Agricultural Chemistry in Harvard University. Nineteenth Edition, Newly Revised. New York : D. Van Nostrand Company. 1899. vii+202 pp. Price, \$1.25 net.

The publication of nineteen editions in thirty years of a scientific book is ample evidence both of the value of the work and of the general appreciation of its value. This is particularly true of a work of this kind when every teacher of qualitative chemistry seems to find it necessary to publish a book covering this course for the special benefit of the pupils in the institution to which he is attached.

The plan of the work is excellent and follows the course which should be pursued by any one beginning the study of qualitative analysis. Beginning with examples of the separation of two elements, the student is led gradually on to the separation of the groups and the different members of each group. The treatment of an unknown substance follows, and so through the entire range of the subject. The descriptions are uncommonly clear and the language is simple and vigorous. The changes from the first revised edition are very slight and are in line of improvement, but some of the old cuts of apparatus are antiquated and below the standard of the rest of the book.

ANDREW A. BLAIR.

BOOKS RECEIVED.

The Compendious Manual of Qualitative Chemical Analysis of C. W. Eliot and F. H. Storer, as revised by W. R. Nichols. Nineteenth edition, newly revised by W. B. Lindsay and F. H. Storer. New York : D. Van-Nostrand Co. 1899. vii+202 pp. Price \$1.25 net.

Wheat. Bulletin No. 83. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky. August, 1899. 20 pp.

The Elements of Blowpipe Analysis. By Frederick Hutton Getman, New York: The Macmillan Co. 1899. x + 77 pp. Price, 60 cents.

The Chemical Composition of American Food Materials. By W. O. At-

water and A. P. Bryant. Bulletin No. 28. (Revised edition.) Washington: U. S. Department of Agriculture. 1899. 87 pp.

Description of a New Respiration Calorimeter and Experiments on the Conservation of Energy in the Human Body. By W. O. Atwater and E. B. Rosa. Bulletin No. 63. U. S. Department of Agriculture. 1899. 94 pp.

Studies on Bread and Bread Making. By Harry Snyder and L. A. Voorhees. Bulletin No. 67. U. S. Department of Agriculture, Washington, D. C. 1899. 51 pp.

A Course in Quantitative Chemical Analysis, Gravimetric and Volumetric. By Nicholas Knight, A.M., Ph.D. New York: A. S. Barnes & Co. 1899. x+110 pp. Price, 80 cents.

Indicators and Test-papers: Their Source, Preparation, Application, and Tests for Sensitiveness. By Alfred I. Cohn, Ph.G. New York: John Wiley & Sons. 1899. ix+249 pp. Price, \$2.00.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THE NATURE OF THE CHANGE FROM VIOLET TO GREEN IN SOLUTIONS OF CHROMIUM SALTS.¹

By W. R. WHITNEY.

Received October 10, 1899.

AN article entitled "The Nature of the Change from Violet to Green in Solutions of Chromium Salts," was published by Venable and Miller in this volume of the Journal, pages 484-496.

As it does not seem that the conclusions drawn in that article are supported by the experimental evidence presented by them, and as I believe that the statements there made are misleading because of the imperfect presentation and discussion of facts previously known, I desire to call attention again to the subject.

The question under discussion concerns the change in composition taking place when a solution of a violet chromium salt, such as chromic sulphate, is heated, the solution then changing in color to green. The following are some of the facts which have been discovered and published by various investigators as evidence for the belief that the green solution, unlike the violet solution, contains a considerable quantity of free sulphuric acid, a conclusion disputed by Venable and Miller.

1. The green solution is strongly acid to all indicators and is

¹ Read before the Columbus meeting of the American Chemical Society, August 21, 1899.

partially precipitated by barium chloride, giving barium sulphate. These facts together are evidence of the presence of some free sulphuric acid.

2. Distillation of the green solution results in an acid distillate, while the dried salt may be heated above 100° C. without loss of acid.¹

3. Dialysis of the green solution gives a product in the diffuse containing proportionately more SO_4 than was obtained by diffusion of the violet solution.²

4. Sulphuric acid has a retarding action on the change from violet to green taking place when the solution is heated. If sulphuric acid is present in the green solution as one of the products arising from the conversion of the violet salt, its addition should retard the conversion in accordance with the law of mass action.

5. Conversely, alkalies accelerate the change from violet to green (Van Cleeff). On the assumption that free acid is present this also would be acquired by the law of mass action.

6. Alcohol poured in a layer over the green solution takes up acid from that solution.³

7. The heat generated on the addition of various quantities of sodium hydroxide to a quantity of the green solution has been carefully measured and the following results obtained: The addition of sodium hydroxide caused at first a generation of heat for each additional portion, exactly equal to that generated when the sodium hydroxide was added to sulphuric acid alone. This relation ceased when a quantity of alkali had been added equal to one molecule of sodium hydroxide to one of chromic sulphate. When more than one molecule (but not when less than one) has been added, the subsequent addition of sulphuric acid brings about a generation of heat. If the first molecule of sodium hydroxide had caused the formation of a chromium hydroxide instead of sodium sulphate in the solution, the addition of acid would have produced a generation of heat. This indicates that there is one molecule of free sulphuric acid for each two molecules of the original chromic sulphate present.⁴

¹ Recoura : *Compt. rend.*, 112, 1440.

² Van Cleeff : *J. prakt. Chem.*, 23, 58; Dougal : *J. Chem. Soc.*, 69, 1527.

³ Krüger : *Ann. phys. Chem.*, (3), 61, 218.

⁴ Recoura : *Ann. chim. phys.* (7), 4, 494.

8. The electrical conductivity of the violet solution is much less than that of an equally concentrated green solution, the difference being readily explained by the presence of free acid in the green solution, inasmuch as free acids are known to be much better conductors than their neutral salts.¹

9. The electrical conductivity of the green solution is decreased at first by the addition of alkali. This reduction of conductivity ceases as soon as one molecule of sodium hydroxide has been added to each molecule of chromic sulphate of the original solution, while still further addition of the hydroxide causes an increase in the conductivity.¹ This can hardly be explained otherwise than by the assumption that free acid is present and that it is neutralized by the alkali. If no chemical change occurred when sodium hydroxide was added to the green solution the electrical conductivity would, of course, increase. It is hard to see how it could diminish to any considerable extent except in case free acid is present. The hydrogen ions of this acid and the OH ions of the base forming as they do undissociated water molecules and thus ceasing to take part in the electrical conductivity, would, however, account for the considerable reduction in conductivity observed. The above is a fact corresponding perfectly with the discovery of Recoura from his thermochemical measurements, that one free sulphuric acid molecule is present in the green solution of two molecules of chromic sulphate. Sodium hydroxide added to the violet sulphate solution does not produce the above effect except to a very slight extent; the conductivity of the solution increases after a very small addition of the hydroxide.

10. Finally, the green solution inverts cane-sugar solutions and hydrolyzes methyl acetate, and to the same extent as a solution of sulphuric acid containing an amount of acid corresponding to one molecule for two of original chromic sulphate. All investigations previously made have led to the conclusion that this inverting or catalyzing action does not occur with neutral salts and in acid solutions is approximately proportional to the concentration of the hydrogen ions present.² Violet solutions of chromic sulphate do not possess this hydrolyzing power.¹

¹ Whitney: *Ztschr. phys. Chem.*, 20, 40.

² See J. H. Long: *This Journal*.

These facts Venable and Miller treat in the following manner: "We think the experimental data of these authors do not afford sufficient and satisfactory evidence to serve as a basis for their conclusions that free sulphuric acid exists in the solution. The methods adopted are very indirect and the results capable of other explanation." Unfortunately, however, no other explanations are suggested by the authors, nor is the reasoning of other investigators in this field refuted to the slightest degree by them.

The entire experimental work of the authors bearing on this matter, which they apparently consider to outweigh the above evidence showing the presence of free acid, consists of a single experiment, which is as follows: Decinormal ammonia was added to a violet and to an equivalent green chromic sulphate solution until the first appearance of a permanent precipitate was noted, and it was found that the two required, within about four per cent., the same volume of the ammonia solution. They seem to conclude, therefore, that the two contain the same amount of acid, and apparently have overlooked the significance of the fact stated on a preceding page of their article and previously announced by Van Cleeff, "Sodium, potassium, or ammonium hydroxide or the carbonate readily turned the violet solution green." This change in color, moreover, precedes the formation of the permanent precipitate. It seems superfluous to add that if the ammonia changes the violet to a green solution it is an unsuitable reagent to use in attempting thus to distinguish the acidity of the solutions.

NEW EXPERIMENT ON THE FREE ACID.

I have performed the following experiment, which again proves the presence of the stated amount of free acid in the green solution.

In order to separate the free acid from the green solution of the chromium compound, in which it cannot be titrated with alkali owing to the progressive decomposition of the chromium compound, the plan was adopted of passing an electric current through the solution and thus causing a removal of the acid from the chromium into an adjoining solution of a simple salt, owing to the more rapid migration of the hydrogen ions.

In order to avoid stirring and convection currents in the solution, the artifice of gelatinizing the solution as employed by Arrhenius,¹ Oliver Lodge,² and Whetham³ was made use of.

It having been found by Arrhenius that the effect on the velocity of migration of different salts by the solidification of the solution with gelatine was not great, and was practically constant for different substances in the same jelly, Whetham employed the method in obtaining the specific velocities of migration of various ions, finding, for example, that the hydrogen ion moved about five times as fast as the chlorine and three times as fast as the next in order to itself, the hydroxyl ion.

It was on this difference in velocity of migration that it was hoped a method of separation could be based.

The experiment was first carried out as follows: An aqueous solution of 0.5153 gram of $\text{Cr}_2(\text{SO}_4)_3 \cdot 14.8\text{H}_2\text{O}$ was boiled thirty minutes to change the salt completely into the green modification. This was made into a jelly by use of two per cent. of agar-agar. A large quantity of two per cent. agar-agar jelly was also prepared containing a few per cent. of potassium sulphate and some methylorange as indicator. A straight glass tube about forty cm. long and having an internal diameter of about two cm. was corked at one end, placed perpendicularly, and filled nearly half full of the neutral potassium sulphate agar-agar solution, which was then allowed to solidify. The melted agar-agar solution containing the green chromium compound was then poured into the tube and allowed to solidify on top of the first jelly. When this was in turn solid, the tube was filled to the end with more of the potassium sulphate jelly. There was thus obtained a solidified solution of the green compound about three cm. long between similar solutions of neutral salt. The cork having been removed, the ends of the tubes were fitted with glass elbows and the whole arranged horizontally with the elbows turned upwards. In one of these elbows was placed an aqueous solution of zinc sulphate and a zinc electrode, in the other copper sulphate solution and a copper electrode. Thus, there could be no acid or alkali produced at the electrodes. The whole apparatus was surrounded by cold water to prevent the liquefaction of the agar-agar due to the

¹ Kongl. Vetenskaps.-Akademiens Föredhandlingar, (1885).

² B. A. Report, 395 (1886).

³ *Phil. Mag.*, 392 (1894).

heat of the electric current. The current from a 110-volt circuit was passed through a thirty-two candle-power lamp and this apparatus in series, the copper pole being made the cathode. The current resulting was probably not far from three-quarters of an ampere. The jelly adjoining the green zone towards the cathode immediately began to redden and the resulting red zone augmented slowly towards the cathode, as the methyl orange was effected by the advancing acid. After four and a half hours, when the methyl orange had been reddened for a distance of 16.5 cm. the current was interrupted and the jelly pressed out of the tube. The reddened portion was cut out and divided into two parts. One constituting the end towards the cathode had a length of 14 cm. and the other adjoining the chromium compound a length of 2.50 cm. These portions were extracted with cold water until the jelly contained no more acid and the resulting extracts titrated. The larger portion required 12.95 cc. of sodium hydroxide (0.0504 normal) solution, the smaller 0.63 cc. of the same solution, showing that the migrating acid was principally in the forward part of the moving reddened zone. The total quantity of sulphuric acid thus found was 0.0355 gram, while a calculation on the basis of Recoura's hypothesis, *i. e.*, one molecule of free acid for two of original chromic sulphate, requires 0.0379 gram. In other words, 88.4 per cent. of the acid hypothetically present had been obtained. Owing to the long period necessary for this migration it was certain that the green compound reverted somewhat to the violet, thus reducing the quantity of free acid, and in fact the movement of a narrow violet zone due to the chromium ions was plainly visible between the green and reddened portions of the jelly, the green color having moved no more than to the small extent attributable to ordinary diffusion.

The above experiment was repeated with chrome alum under improved conditions. This time the jelly was removed after being in use between two and three hours. It was separated into its differently colored parts, and that containing chromium was this time reheated to reconvert any violet chromium sulphate into the green modification. It was then returned to the tube as before, together with fresh portions of the neutral potassium sulphate jelly. On the passage of the current a faint red zone was produced, but not nearly so marked as before, and

it was soon evident that the acid had all been separated from the chromium compound. The total quantity of acid obtained on extraction of the reddened portions of jelly was titrated as before.

In this case 0.8125 gram of chrome alum had been used, corresponding theoretically to 0.0399 gram of free sulphuric acid. There were 16.3 cc. of the alkali solution used to neutralize the free acid, which corresponds to 0.0402 gram of sulphuric acid instead of 0.0399. This is as close an agreement as the process could be expected to give. Experiment showed that no measurable action of free acid on the agar-agar takes place under the conditions of the above process.

It was now desirable to perform a similar experiment with the violet solution. On making the jelly containing the alum as before, it was found that the return of the violet color which was changed to green by the melting of the agar-agar solution, required at least weeks for its completion, and therefore for this purpose the solution of the alum in the hot melted agar-agar had to be abandoned. It was found, however, that on placing the solid powdered alum between two pieces cut from a jelly cast in the tube above described, the substance dissolved quite readily, and rapidly diffused throughout the pieces of jelly. Such a plug of the jelly, containing two-tenths gram of alum, was placed in the center of the tube with the neutral potassium sulphate jelly as before and the current passed through the whole for an hour. It failed to yield sufficient acid to affect the indicator, though the relatively slow migration of the chromium ions was evident. These experiments therefore show the presence of the free acid in the green sulphate solutions and determine that its amount corresponds to the hypothesis of Recoura.

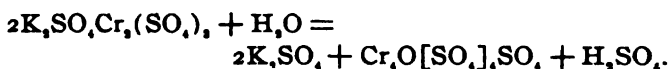
THE NON-PRECIPITABLE SULPHATE.

Favre and Valson¹ fractionally precipitated the green chrome alum solution by adding to it successively portions of barium chloride solution equivalent to one-quarter of the quantity theoretically necessary to precipitate all the SO_4 present. The first and second quarters were immediately and completely used up in precipitating barium sulphate, while the third quarter produced a very slowly appearing cloudiness, which became an

¹ *Compt. rend.*, 74, 1032.

actual precipitate only after the expiration of a considerable time. The heat generated in this reaction was likewise measured. For the first, second, and third quarters of barium chloride added, 4104, 4102, and 146 calories, respectively, were generated. Thus, these authors were led to conclude that only half of the sulphuric acid actually present is immediately precipitable.

Recoura¹ simply states that he has confirmed this conclusion, and advances the following reaction and formulas as representing the compounds actually in the green solution :



In this case, the SO_4 in the brackets assumed to be a part of a positive radical attached to a single SO_4 , and forming one-half of the total SO_4 present would be the non-precipitable portion. Venable and Miller also attempted to investigate the point quantitatively. As they were unable to filter the precipitated sulphate, because of its finely divided condition, until after the lapse of about twenty-four hours, it is not surprising that they obtained in the precipitates about ninety per cent. of the total SO_4 present. To obtain a satisfactory separation of the immediately precipitable sulphate, it is necessary that the barium sulphate at first thrown down should be filtered at once, for the remainder of the SO_4 present will be slowly precipitated, as described by Favre and Valson, owing to the gradual return of the green to the violet compound.

The following quantitative evidence on this point has been obtained :

Two solutions were made by dissolving 0.5982 and 0.4605 gram of recrystallized chrome alum, each in about 100 cc. of water at 0° C. An excess of a four per cent. barium chloride solution, also at 0° C., was slowly added to each from a burette, the solutions being constantly stirred. The precipitates of barium sulphate were filtered and washed immediately. They were perfectly white and on ignition weighed 0.5508 and 0.4249 gram, respectively. This corresponds in each case to 98.7 per cent. of the SO_4 theoretically present in the alum. The filtrates

¹ *Ann. chim. phys.* (7), 4, 502.

yielded no further precipitates on being boiled. This shows that the SO_4 can be precipitated immediately from the ordinary violet solution of chrome alum at 0°C .

The green solutions to be precipitated were made by dissolving known weights of the alum in water and boiling for half an hour. After being cooled to 0°C . these were precipitated as above, more of the precipitant being added in each case than would be necessary to throw down all the sulphuric acid present in whatever form. The resulting precipitates collected on double filter-papers were of different shades of green and evidently contained varying quantities of the chromium compound. After thoroughly washing these precipitates they were digested with boiling dilute hydrochloric acid, the acid evaporated almost to dryness, and the precipitates, after being digested with boiling water, were filtered. These were then fused with sodium carbonate and the sulphate in the filtered and acidified solution of the fusion, reprecipitated. The following table contains the results:

Alum.	Total BaSO_4 calculated.	<i>a.</i>	BaSO_4 found. <i>b.</i>	<i>c.</i>	Precipitated SO_4 . Per cent.
0.8064	0.7531	0.4336	0.4129	54.9
0.7255	0.6776	0.3787	0.3397	50.1
0.5062	0.4728	0.2557	0.2515	53.2
0.6470	0.6042	0.3490	0.3409	56.4
0.8235	0.7690	0.4102	0.4042	52.5
0.9160	0.8554	0.4564	0.4489	52.4

The values under *a* give the weights of the greenish precipitates at first obtained, so far as they were determined. All of these precipitates yielded considerable quantities of chromium and of sulphuric acid to the hydrochloric acid used in their purification. Under *b* are the weights of the precipitates after the hydrochloric acid treatment, and under *c* the weights of barium sulphate after fusion with the sodium carbonate and reprecipitation. These latter were used in the calculation of the percentages of precipitable sulphuric acid which appear in the last column.

When the difficulties connected with this determination are taken into account, it is probable that exactly one-half of the sulphuric acid of a green solution of chrome alum is present in a form which does not readily yield the SO_4 ion. The fact

that the filtrates from the above precipitates remained perfectly clear for periods of from thirty to ninety minutes, varying with the temperature at which they were kept, is worthy of note.

It is therefore clear that all experimental evidence thus far points to the correctness of Recoura's peculiar symbols representing chromium compounds, for here in the case of the chromé alum solution, the free acid, as well as the directly ionizable sulphuric acid radicals, has been shown to correspond in quantity with the requirements of the symbol,



i. e., one-half of the SO_4 exists as ordinary sulphate, including one-eighth as free acid, and the other half in a condition of considerable stability and non-precipitable, at ordinary temperatures.

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THE DETERMINATION OF THE BROMINE ABSORPTION OF OILS.

BY PARKER C. MCILHINEY.

Received September 22, 1899.

SOME time ago the writer suggested a method of fat analysis, having the same end in view as the Hübl process; *viz.*, the determination of the unsaturated constituents of fats and oils.¹ Since then Hehner² has called attention to the fact that Allen³ had previously described a similar method of analysis for shale oils. This fact had escaped the writer's attention and his apologies are due to Mr. Allen for the omission of credit where it belonged.

Further experience with the method has confirmed the belief that its results are more valuable than those given by the Hübl process, and recently it has been found possible to so modify its details that it can be carried out more easily and expeditiously. The method consists briefly in adding to a weighed portion of the fat or resin in a stoppered bottle, an excess of standard solution of bromine in carbon tetrachloride, and, after the reaction between them has taken place, determining the excess of bromine

¹ This Journal, 16, 275.

² *Analyst*, 20, 40 (1895).

³ *Commercial Organic Analysis*, second edition, 2, 383.

by adding an aqueous solution of potassium iodide and titrating with sodium thiosulphate. Any hydrobromic acid which may have been formed in the reaction is determined in the aqueous solution. The percentage of bromine found as hydrobromic acid is called the bromine substitution figure, and the total percentage of bromine absorbed, less twice the bromine substitution figure, gives the bromine addition figure.

When the original article was written the rapidity with which bromine reacts with fats was not appreciated. On investigation it was proved that if the fat is treated with double the quantity of bromine with which it can combine, the reaction between them is complete within one minute; no higher addition figures were obtained when the tests were continued for a number of hours. This agrees with the statement of *Hehner and Mitchell* that the reaction is instantaneous. The process can therefore be carried out very rapidly.

Several objections to the *Hübl* process may be stated as follows:

1. The solution of iodine and mercuric chloride is not a stable one. When freshly prepared, its action is apt to be erratic for the first few hours and after that its strength steadily decreases. The result of this is that several hours must be devoted to the preparation of the reagent before the analysis proper can be carried on.

2. The reaction between the reagent and oil is not instantaneous; in fact several hours are required for its completion. With drying oils probably eighteen hours are required. This further delays the analysis.

3. The process does not distinguish between iodine absorbed by addition and that absorbed by substitution. In the case of pure glycerides this is not so serious a defect as in the case of hydrocarbon oils and resins, which absorb halogen mostly by substitution of the halogen for hydrogen. The time allowed for the reaction affects the amount of halogen absorbed to a much greater extent with the latter class of substances than with glycerides, so that no definite *Hübl* figures can be given for them except as a time is arbitrarily fixed for the reaction. This defect of the method is very marked in the case of rosin. Another result of the lack of distinction between addition and

substitution in the Hübl process is that substances whose behavior toward halogen is essentially different, such as rosin and linseed oil, may give the same Hübl figures.

The superiority of bromine over iodine as a reagent in fat analysis has been shown by many investigations during the last three years. A process devised by Hehner and Mitchell,¹ in which the heat developed by the reaction between bromine and oils is measured, appears to possess very decided merits on the score of rapidity, especially if a large number of samples are to be examined at one time. This advantage is not apparent, however, if only a few samples are to be examined. It is open to one of the same objections as the Hübl process in failing to distinguish between addition and substitution and further the errors of the thermometer reading are multiplied by five and a half in calculating the Hübl figure. It would seem to the writer, although he has had no personal experience with it, that its advantages in rapidity are also possessed by the method which forms the subject of this paper.

The method formerly employed for determining the bromine substitution figure, was to determine the acidity to methyl orange of the aqueous liquid separated from the carbon tetrachloride after the titration with thiosulphate. Experiments were made to compare the results obtained by using methyl orange and by lacmoid and by determining the acid iodometrically with potassium iodate and iodide. The results of the tests showed that in the case of many oils there was little or no difference between the figures obtained. In the case of others, however, the end-reaction with methyl orange was indistinct, and lacmoid gave high figures. This is undoubtedly due to the presence of fatty acids in the solution. The iodometric determination in the same way as used by Schweitzer and Lungwitz,² is therefore to be recommended, especially as it involves no separation of the aqueous portion from the carbon tetrachloride and the same thiosulphate solution serves for determining both the excess of bromine and hydrobromic acid.

The process as at present used is as follows: A quantity of the oil to be analyzed is weighed into a glass-stoppered bottle,

¹ *Analyst*, 20, 49, 146 (1895); *J. Soc. Chem. Ind.*, 16, 87, 309 (1897); *This Journal*, 14, 378 (1896).

² *J. Soc. Chem. Ind.*, 14, 130 (1895).

ten cc. of carbon tetrachloride added to dissolve the oil, and twenty cc. of third-normal bromine in carbon tetrachloride added from a pipette. It is not found necessary in filling the pipette with bromine solution to use any special arrangement to prevent the introduction of bromine vapor into the mouth. Only a rubber tube is necessary. Another pipette full of solution should be added to ten cc. of carbon tetrachloride, and this blank titrated with thiosulphate to determine the strength of the bromine solution. The test itself need be allowed to stand only one or two minutes before adding twenty to thirty cc. of ten per cent. solution of potassium iodide, the amount necessary depending upon the excess of bromine present. An excess, of course, does no harm. In order to prevent any loss of bromine or hydrobromic acid which would probably occur on removing the stopper of the bottle, a short piece of wide rubber tubing, of the sort used for Gooch crucibles, is slipped over the lip of the bottle so as to form a well around the stopper. It is advisable, also, to cool the bottle by setting it into cracked ice in order to produce a partial vacuum in the interior. Into the well formed by the rubber tubing is poured the solution of potassium iodide and the stopper opened slightly. If the bottle has been cooled with ice the iodide solution will be sucked into the bottle, and if it was not cooled some of the air from the interior of the bottle will bubble through the iodide solution, being thereby washed, and allow the iodide solution to enter the bottle. When sufficient iodide solution has been introduced the bottle is agitated to insure the absorption of the bromine and hydrobromic acid by the aqueous solution. The iodine now present is titrated with tenth-normal sodium thiosulphate and when the titration is finished five cc. of a neutral two per cent. solution of potassium iodate is added. This liberates a quantity of iodine equivalent to the hydrobromic acid formed and on titrating this iodine the bromine substitution figure may be calculated. The solution of potassium iodate should be tested for acidity by adding a measured quantity to a solution of potassium iodide and if any iodine is liberated it should be determined with thiosulphate and a suitable correction introduced into the calculation. The potassium iodide, the thiosulphate solution, and the water used should all be tested to see that they are neutral.

The reaction between bromine and oil appears to be practically instantaneous as far as the bromine taken up by addition is concerned but it seems likely that substitution is distinctly affected by the length of time that the oil and bromine are allowed to remain in contact. The extent to which time affects the substitution figure has not yet been accurately determined, but it is not likely that in ordinary work any serious error is introduced in this way. Experiments to determine accurately the effect of time upon the substitution figure have been undertaken and will be reported later.

For the process in its present form the following advantages may be claimed :

1. The standard solution of bromine is not subject to change on keeping ; therefore it may be kept on hand ready for use at short notice ; further, it is very easily prepared.
2. The process requires only such time as is necessary for the weighing and the titration, no time being lost in preparing standard solutions or waiting for completion of the reaction between bromine and oil.
3. The absorption of halogen by addition is determined separately from the absorption by substitution, and thus additional information is gained as to the nature of the substance:
4. The solvent used (carbon tetrachloride) is easily recovered, and bromine is cheap, so that the whole process is much cheaper than the Hübl.

The following figures have been obtained upon samples of various oils which are believed to be representative of their respective classes.

The figures given in the last column, obtained by dividing the calculated bromine figures by the actual bromine addition figures, are intended to represent by the amount that they exceed 1,000, the extent to which substitution goes on in the determination of the Hübl figure. Thus 1.103 represents that over and above the iodine absorbed by addition; 10.3 per cent. of this amount was absorbed by substitution.

	Hübl figure.	Bromine calculated from Hübl.	Per cent. of bromine absorbed.	Bromine addition figure.	Bromine substitution figure.	Bromine from Hübl divided by bromine addition figure.
Raw linseed oil, several years old, 1.....	166.9	105.2	98.4	95.4	1.5	1.103
Raw linseed oil, several years old, 2.....	157.3	99.1	99.2	92.0	3.6	1.000
Raw linseed oil, 3.....	184.2	116.1	116.1	109.6	3.4	1.059
" " " 4.....	178.6	112.6	112.6	102.1	3.2	1.102
" " " 5.....	185.9	117.2	113.2	109.2	2.0	1.072
" " " 6.....	186.3	117.0	112.2	106.5	2.9	1.098
" " " 7.....	104.5	99.9	2.3
" " " 8.....	115.1	109.5	2.8
" " " 9.....	114.6	109.4	2.6
Av. omitting Nos. 1 and 2	183.8	115.7	112.0	106.6	2.7	1.083
Boiled linseed oil, 1....	180.4	113.7	106.0	100.8	2.6	1.126
" " " 2....	183.3	115.5	110.8	105.8	2.5	1.091
" " " 3.....	105.4	101.2	2.1
" " " 4.....	110.0	103.2	3.4
" " " 5.....	109.8	105.2	2.3
" " " 6.....	113.6	103.0	5.3
" " " 7.....	109.2	103.8	2.7
" " " 8.....	110.8	101.0	4.9
Averages.....	109.5	103.0	3.2
Petroleum neutral oil, sp. gr. 0.8436.....	14.4	6.4	4.0
Third run rosin oil, 1	197.6	16.4	90.6
" " " " 2 ..	63.9	40.3	92.3	7.7	42.3	5.231
"Mystic" brand rosin oil	93.7	6.3	43.7
"Java" boiled rosin oil ..	73.3	46.2	101.9	8.3	46.8	5.685
Menhaden oil, 1.....	178.8	112.7	114.5	96.5	9.0	1.169
" " 2.....	170.4	107.4	107.3	92.3	7.5	1.164
" " 3.....	175.4	110.6	110.1	97.9	6.1	1.129
Averages	174.9	110.2	110.6	95.6	7.5	1.154
Corn oil, 1	76.2	73.8	1.2
" " 2	75.8	73.2	1.3
" " 3	75.4	71.6	1.9
Averages.....	75.8	72.9	1.5
Cottonseed oil	65.8	62.2	1.8
Turpentine	266.1	166.1	50.0
Benzine, turps. substitute, 1, sp. gr. 0.741	51.5	15.5	18.0
Benzine, turps. substitute, 2, sp. gr. 0.733	6.3	2.7	1.8
Window glass rosin.....	161.4	8.0	76.7
Black rosin	135.4	5.4	65.0
Ceylon cocoanut oil....	5.36	4.7	0.33
Tallow ren'd in lab'ratory	24.0	21.48	1.26
Hard paraffin	3.55	1.43	1.06

THE DIRECT DETERMINATION OF AVAILABLE PHOSPHORIC ACID.

BY F. P. VRECH.

Received September 4, 1899.

THE direct determination of available phosphoric acid is not new, being official in several of the European countries. In this country, however, it has not met with favor, probably because the citrate method is not official here. The necessity of destroying the organic matter before precipitating with molybdate solution precludes the use of the molybdate method.

In 1893 Ross presented a method¹ for the direct determination of the reverted phosphoric acid. While the aim of this method met with hearty approval from the official chemists, the method itself did not, owing to some difficulties met with in the manipulation, and more particularly to the fact that it did not give results agreeing with the official method.² Agreement could hardly be expected seeing that the method did not account for that phosphoric acid removed in the water used in washing the citrate insoluble. Believing that this last-mentioned fact, *viz.*, that the Ross method did not account for the phosphoric acid contained in the wash-water of the official method, is the principal cause of the difference in the results by the two methods, in 1895, the writer did some work with the view of proving his hypothesis. This work consisted of the determination of the water-soluble phosphoric acid by the volumetric method, as modified and carried out by the writer;³ the direct determination of the citrate-soluble by the citrate method, in fifty cc. of the citrate filtrate, and the determination of that removed by washing the citrate-insoluble residue, using the modified volumetric method. The sum of these three results should equal the available phosphoric acid by the official method.

It is perhaps sufficient to say that the citrate method at that time and later⁴ gave satisfactory results on sixty or seventy samples. The results of the comparison are given in the table.

¹ U. S. Department of Agriculture, Division of Chemistry, Bulletin 38, p. 17.

² U. S. Department of Agriculture, Division of Chemistry, Bulletin 43, p. 72; and Bulletin 47, p. 81.

³ This Journal, 18, 389, and U. S. Department of Agriculture, Division of Chemistry, Bulletin 49, p. 61.

⁴ U. S. Department of Agriculture, Division of Chemistry, Bulletin 49, pp. 61, et seq.

AVAILABLE PHOSPHORIC ACID.

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	Direct method.					Official method.	
	Soluble. Per cent.	Reverted. Per cent.	Wash. Per cent.	Available. Per cent.	Total. Per cent.	Available. Per cent.	Total. Per cent.
1	10.13	3.60	0.24	13.97	16.15	14.00	16.18
2	12.46	2.96	0.17	15.59	16.09	15.49	15.99
3	10.88	3.68	0.21	14.77	16.10	14.79	16.12
4	4.80	5.13	0.29	10.22	11.70	10.14	11.62
5	8.25	2.65	0.47	11.37	12.17	11.24	11.97
6	7.56	3.61	0.26	11.45	14.48	11.58	14.64
7	8.08	2.24	0.25	10.57	12.79	10.64	12.75
8	7.00	4.76	0.37	12.08	16.48	12.21	16.54
9	9.03	3.12	0.28	12.43	13.86	12.31	13.74
10	1.18	6.22	0.68	8.08	12.74	8.03	12.69
11	1.08	6.35	0.99	8.42	12.96	8.32	12.86
12	3.10	4.88	1.48	9.46	15.41	9.50	15.45
13	5.10	1.73	0.21	7.04	8.16	7.03	8.35
14	8.87	2.10	0.09	11.06	11.39	10.86	11.19
15	4.75	2.30	0.39	7.44	8.84	7.45	8.85
16	4.97	2.98	0.38	8.33	10.72	8.44	10.83
17	4.27	2.34	0.19	11.80	12.53	11.82	12.55
18	7.47	3.34	0.30	11.11	13.28	11.23	13.40
19	5.55	3.59	0.40	9.54	14.48	9.70	14.64
20	7.50	2.06	0.16	9.72	11.92	9.70	11.90

Nos. 1, 2, and 3 were dissolved S. C. rock.

Nos. 4, 5, and 6 were dissolved S. C. rock and potash.

Nos. 7, 8, and 9 were dissolved animal bone.

Nos. 10, 11, and 12 were raw bone.

Nos. 13, 14, 15, 16, 17, 18, 19 and 20 were compounded for this work and were complete fertilizers.

The two methods gave practically the same results on availables and on totals. The work also shows very plainly why the Ross method differs from the official, from 0.09 per cent. to 1.48 per cent. being removed and accounted for in the wash-water of the official method that could not be accounted for by the Ross method. Of course the amount removed by the wash-water will vary somewhat in the hands of different analysts, according as they wash the citrate-insoluble much or little. It is the practice of the writer to wash until the filtrate and washings amount to about 250 cc.

At this point pressure of other work necessitated the dropping of this, and nothing more was done until the present summer, when it was determined to extend the work somewhat.

A comparison of the official method with the citrate and the molybdate methods, precipitating with magnesia mixture and

with molybdate solution, respectively, in the mixed filtrates, containing the water-soluble and the citrate-soluble, was undertaken.

The method pursued was as follows: the water-soluble, extracted as usual, was received in a 500 cc. flask, graduated roughly at 250 cc. and containing five to ten cc. nitric acid. The citrate-soluble was then extracted as usual, the filtrate and washings received in the flasks with the water-soluble. After cooling, the volume was completed, shaken, filtered, and in aliquots of 100 cc. the phosphoric acid was determined by each method, the molybdate solution being added directly to the solution without destroying the organic matter, but the precipitates were allowed to stand over night before filtering. The determinations were completed as usual. The samples were carefully selected to represent most classes of goods found on our markets. Most of them contained organic matter, some in considerable quantities.

		Available official method. Per cent.	Available direct. Molybdate method. Per cent.	Citrate method. Per cent.
21	Dissolved S. C. rock	15.87	15.84	15.40
22	" " " "	14.40	14.51	14.50
23	" " " " and potash	13.45	13.45	13.24
24	" " " "	14.82	15.04	14.53
25	" " " "	15.60	15.66	15.47
26	" " " " and potash	11.78	11.90	11.76
27	" " " " " "	14.11	13.95	13.94
28	" " " " " "	11.96	11.80	11.6.
29	" " " " " "	9.09	9.06	8.9c
30	" " " " " "	10.44	10.36	10.24
31	" " " " " "	13.09	13.08	12.63
32	" " " " " "	9.02	8.87
33	" " " " " "	9.58	9.60
34	" " " " " "	10.01	10.13
35	Dissolved animal bone	10.58	10.65	10.35
36	" " " "	12.31	12.50	12.14
37	" " " "	14.27	14.10	13.86
38	Complete	7.71	7.67	7.13
39	"	11.49	11.54	11.32
40	"	9.61	9.71	9.86
41	"	7.39	7.27	7.05
42	"	9.08	9.03	8.90
43	"	10.14	9.96	9.84
44	"	9.70	9.87

	Available official method. Per cent.	Available Molybdate method. Per cent.	direct. Citrate method. Per cent.
45 Complete, contains great deal tankage	5.27	5.31
46 " " " "	8.51	8.39
47 " contains bone-black	6.46	6.64
48 " " blood	5.09	4.99
49 " " " "	8.18	8.18
50 " " " "	7.91	7.75
51 " " " "	7.37	7.35
52 " contains great deal fish	7.44	7.59
53 " " " "	9.38	9.36

The results by the citrate method were unexpectedly low. In the writer's hands this method had always given satisfactory results, even on low percentages. It is probable the low results were due to an excess of citrate, twenty to thirty cc. more having been added to each sample. This addition was unnecessary, and better results when more citrate was not added, leads to the belief that this additional citrate was the cause of the low results: No time remained, however, to confirm this opinion.

The results by the molybdate method were good. It was feared that the organic matter present would prevent the complete precipitation of the ammonium phosphomolybdate. To insure complete precipitation the samples were allowed to stand over night before filtering. In view of the results it is to be regretted that there was no opportunity for the determination of the time required for the complete precipitation of this salt under these conditions. It is probably not over two hours at 65° C.

Notwithstanding the oft-repeated statement that salts of organic acids and organic matter generally prevent the complete precipitation of ammonium phosphomolybdate, the molybdate method is used to determine soluble phosphoric acid in the presence of what organic matter may be dissolved by the water used in the extraction. In the Wagner method¹ for basic slag, we precipitate with molybdate solution in the presence of three grams of citric acid. Lorenz² precipitates in the presence of two per cent. of citric acid to prevent contamination with magnesia. Jüptner³ uses as much as 100 grams of tartaric acid per liter of

¹ Principles and Practice of Agricultural Analysis, 2, 78.

² *Ibid.*, 2, 54.

³ Abstract Experiment Station Record, 6, 610.

molybdate solution to prevent the precipitation of iron and the separation of molybdic acid. The successful use of the molybdate method in these cases seems to warrant the conclusion that we are needlessly alarmed at the presence of, at least, some forms of organic matter in phosphate solutions.

The direct determination of the available phosphoric acid possesses several advantages. Only one determination is required instead of two as by the present method. The probable error is reduced one-half. We can also determine the soluble, reverted, insoluble, and total phosphoric acid in one sample and with one weighing where it now takes two samples and two weighings.

The saving of time effected by this method is of considerable importance in control and in factory laboratories, whether we use the citrate or the molybdate method, and it is hoped that the subject will receive further attention.

LABORATORY OF THE MARYLAND AGRICULTURAL COLLEGE,
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NOTE UPON THE DETERMINATION OF NITROGEN IN FERTILIZERS CONTAINING NITRATES.

BY F. P. WEITCH.

Received September 4, 1899.

JOHNSON¹ describes a modification of the Gunning method². In this modification potassium sulphide alone is used in the place of potassium sulphate and sodium thiosulphate.

In Johnson's hands the average difference between the methods is 0.02 per cent., the modification giving the higher average.

The writer has used this modification, carried out in a slightly different manner, with very satisfactory results. To the nitrate in the digesting flask are added thirty-five to forty cc. sulphuric acid containing thirty-four grams salicylic acid per liter. Allow to stand in the cold until the nitrate is dissolved. Add six or seven grams of finely broken potassium sulphide, heat over a low flame for fifteen minutes, then over the full flame until clear. Cool and distil as usual. The following are all the results I have obtained by this method.

¹ This Journal, 18, 1102.

² U. S. Department of Agriculture, Division of Chemistry, Bulletin 46.

No.	Gunning. Per cent.	Modification. Per cent.	No.	Gunning. Per cent.	Modification. Per cent.
608	{ 3.70 3.75	3.84	767	2.69	2.68
648	4.45	4.45	782	2.64	2.59
659	2.73	2.90	786	1.24	1.18
719	1.48	1.52	793	2.34	2.39
722	3.15	3.09	808	1.98	2.05
723	1.77	1.81	809	1.11	1.07
725	2.73	2.81	819	2.18	2.13
727	2.51	2.52	820	2.27	2.32
731	2.25	2.25	833	2.76	2.83
733	2.90	3.00	888	4.26	4.18
738	6.62	6.50	917	3.07	3.19
742	{ 5.99 5.75	{ 5.85 5.88	919	2.15	2.17
747	4.30	4.42	924	3.58	3.58
755	3.12	3.22	927	1.91	1.84
756	1.96	2.05	928	2.61	2.58
757	2.88	2.97	933	3.34	3.26
			941	2.90	3.04

Average difference + 0.017.

The greatest difference between the methods is 0.17 per cent. and the average difference is 0.017 per cent. It is advisable to use a little more sulphuric acid in the digestion than is used in the Gunning method. There was no trouble with foaming, turning up the lamps being the only attention required. Time of digestion was about one and a half hours, being about a quarter of an hour longer than in the Gunning method. The modification seems to give as good results, requires fewer chemicals and less attention than the Gunning method, but requires a little longer digestion.

[CONTRIBUTION FROM THE LABORATORY OF AGRICULTURAL CHEMISTRY,
OHIO STATE UNIVERSITY.]

NOTES ON TESTING SOILS FOR APPLICATION OF COMMERCIAL FERTILIZERS.¹

BY H. A. WEBER.

Received September 28, 1899.

FOR more than twelve years of active service in connection with farmers' institutes, the writer endeavored to impress upon the farmers the necessity of a more rational method in the

¹ Read before the meeting of the American Association for the Advancement of Science, August 26, 1899.

use of commercial fertilizers, in order to avoid the useless expenditure of money for plant food which their soil did not require. The means for reaching this result were fully explained, but with few exceptions farmers could not be induced to make for themselves the ordinary field experiments, which alone could inform them of the needs of their soil, and indicate what fertilizers to buy for their fields.

In 1885 the writer instituted a series of experiments with soil in sewer pipes for the purpose of securing a method, by which these soil tests could be made for the farmers at the Ohio State University.¹

The sewer pipes employed were fifteen inches in diameter and the amount of soil required was about 600 pounds. Subsequently it was found, that by the use of six-inch tiles, the amount of soil required could be reduced to seventy-five pounds with equally satisfactory results. The soils were collected in accordance with the following directions:

1. Never send a sample of soil from a field which without fertilizers is capable of yielding a full crop. On a soil of this nature commercial fertilizers will not pay.

2. Never send a sample from a field, which is not in a good, high state of cultivation; *i. e.*, which is not well drained, and where the soil when cultivated is not deep and pulverulent. Commercial fertilizers cannot counteract bad physical conditions of the soil.

3. Never send a sample from a meadow or clover sod, but always from fields that are under cultivation.

4. If a field is in a high state of cultivation and still fails to produce more than half a crop, there is good reason to believe that the soil is deficient in one or more of the essential ingredients of plant food. From such a field an average sample of soil should be sent for testing. In order to collect an average sample of the soil proceed as follows:

Begin at one end of the field and cross it back and forth at intervals of eight or ten paces until the other end is reached. While thus crossing dig a square hole with a spade, every eight or ten paces, down to the subsoil. Cut off a slice about two inches thick from the surface down to the subsoil and throw it

¹ See Fourth Annual Report, Ohio Agricultural Experiment Station, p. 231.

into a wagon-bed. Better still cut out a core of soil with a post-hole digger at each point. Avoid all local contaminations, as the droppings of cattle, piles of decaying vegetable matter, etc. Remove any trash from the surface by scraping before digging the hole, or sinking the post-hole digger. Also avoid all low places in the field, especially if they are filled with black soil or leaf mold. Thoroughly mix the soil thus collected and send not less than seventy-five pounds for testing. The test is made in the following manner:

Ordinary six-inch tiles are placed into large Wagner pots, which contain enough clean sand so that the top of the tiles will be on a level with the top of the pots. The whole is then filled with sand with the exception of the upper seven inches of the tiles. The sand is then thoroughly drenched with rain or condensed water. The empty portion of the tiles are next filled to within an inch of the top with the thoroughly mixed sample of soil, the fertilizer is added and incorporated with the upper portion of the soil by stirring, moistened if necessary, fifteen seeds of oats, spring barley, spring wheat, or other grain are distributed uniformly over the surface, and then covered with enough of the dry soil to bring the surface of the soil on a level with the top of the tiles. The six-inch tiles, to the depth of seven inches as described, will contain about ten pounds or five kilograms of soil.

Five miniature plots are thus prepared for each soil test. If Wagner pots are not available, a box eighteen inches deep with an opening in the bottom for drainage, and large enough to hold five of the tiles, may be employed. The sand surrounding the tiles is kept moist, by adding water once a week.

The amount and kind of fertilizer to be added to the five plots for each test are as follows:

PLOT 1. COMPLETE FERTILIZER.

	Gram.
Superphosphate	1.0
Potassium sulphate	0.5
Sodium nitrate	0.5

PLOT 2. COMPLETE MINERAL FERTILIZER.

	Gram.
Superphosphate.....	1.0
Potassium sulphate.....	0.5

PLOT 3.

	Gram.
Superphosphate	1.0
Sodium nitrate	0.5

PLOT 4.

	Gram.
Potassium sulphate	0.5
Sodium nitrate	0.5

PLOT 5.

No fertilizer.

As examples of this method of testing soils three experiments recently made will suffice.

The three soils were arranged in series of five plots and fertilized as already described. April 29 fifteen oat seeds were planted in each plot. Plants were up on May 3. No difference in the growth of the plants could be noticed before May 16. At this date plots 1, 2, and 3 were alike in all cases and were in advance of plots Nos. 4 and 5. The plots were thinned out to ten plants per plot. On May 18 each plant of plots 1, 2, and 3 had one side shoot, while plots 4 and 5 had none. The difference in growth between plots 1, 2, and 3 and plots 4 and 5 was very marked. On May 22 the plants of plots 1, 2, and 3 had two side shoots and were all practically alike, while plots 4 and 5, which again were alike, had no side shoots, were much smaller and less vigorous. On May 29 the same relation as to growth existed, except that in the case of soils 1 and 2, plot 2, which contained no sodium nitrate, showed nitrogen starvation, and remained in this condition to the end of the experiment. Plot 2 of soil 3 did not reveal nitrogen starvation in the slightest degree, but was in every respect equal to plots 1 and 2.

The plants of plots 4, which contained potassium sulphate and sodium nitrate, were not larger and not more vigorous at any time during the experiment, than those of plots 5, which contained no fertilizer.

From this it will be seen that soils 1 and 2 were deficient in phosphoric acid and nitrogen, while soil 3 was deficient in phosphoric acid only.

The following recommendations were made in accordance with these results: For soils 1 and 2, superphosphate 300 pounds

and sodium nitrate 100 pounds per acre. For soil 3, superphosphate 300 pounds per acre.

In the place of superphosphate a like amount of fine bone-meal was recommended for fall crops, like fall wheat and rye. In making the tests of soils in this manner it is not necessary to bring the plants to maturity, if time will not permit. Observations made on the growth of the plots during five or six weeks, will give sufficient data to interpret the needs of the soil.

The tests thus carried out are much less laborious than an analysis of the soil would be, and the chemist, who occupies a position, where the demands for soil analyses are frequently made by persons not properly informed in the matter, may often find this method of use in imparting that knowledge to the farmer, which will enable him to apply commercial fertilizers to his soil in a rational manner.

ON THE UNIVERSAL DISTRIBUTION OF TITANIUM.

BY CHARLES BASKERVILLE.

Received September 8, 1899.

THE universal distribution of titanium in the mineral and plant world is practically acknowledged. V. Roussel¹ found it in basalt; Aleksiejew² in certain clays. Holland³ found it in certain igneous rocks. Dunnington⁴ observed its occurrence in the soil of Albemarle County, Va.; later the same writer with McCaleb⁵ found it in sixteen specimens of soil collected from different sections of the United States. Subsequently after having examined a large number of samples of soil collected from all parts of the globe Professor Dunnington⁶ asserted its universal occurrence in the soils of the world.

W. A. Noyes⁷ found it in a number of Arkansas minerals. Hillebrand has shown its presence in a large number of rocks and minerals collected by the United States Geological Survey. Wait⁸ found it in the ashes of several plants and different kinds

¹ *Ber. d. chem. Ges.*, 6, 1417, b.

² *Chem. Ztschr.*, Rep. 1896, 261.

³ *Chem. News*, 59, 27.

⁴ *Proc. A. A. A. S.*, 34, 132.

⁵ *Am. Chem. J.*, 20, 36.

⁶ *Am. J. Sci.*, Dec. 1891; *Chem. News*, 65, 65.

⁷ *J. Anal. Appl. Chem.*, 5, 39.

⁸ This Journal, 18, 402.

of wood, also in coals, bituminous and anthracite. Haywood¹ found traces in domestic strawberries and 0.1088 per cent. in the ash of wild strawberries (*Fragaria Virigiana*). Langenbeck speaks frequently of its occurrence in clays. It has been found by the writer rather widely distributed in the clays of this state.² While Roscoe and Schorlemmer state that "It does not appear to form part of the animal and vegetable kingdom," Wait³ assumes that it is assimilated by plants. The writer⁴ shows its presence in the ashes of peat. As the clay substance therein is comparatively small its presence can scarcely be attributed to that. F. Garrigon found traces in mineral waters.

No statement in the literature has been found of its presence being noted in the ashes obtained from the animal kingdom. The ash from incinerated fresh beef, beef bone, human flesh, and bone free from dirt, have been examined in this laboratory with the following results: Beef bone 0.0195 per cent., beef flesh 0.013 per cent., human bone⁵ a trace, human flesh⁶ 0.0325 per cent. titanic oxide.

A private communication from Dr. J. L. Howe concerning the work of some of his students states that "Toole found titanium in abundance in dead bones, but only traces in fresh bone and muscular tissue, though traces were undoubtedly there." Dr. C. E. Wait in a letter of recent date writes: "Since my note on titanium was published a year or so ago, I have made an examination of a large number of bodies and I believe that element was found in nearly all of them. I have made a large number of estimations of titanium in vegetable bodies, and later took up the examination of animal flesh and bone, and the last piece of work along that line was the examination of human excretory products."

The universal distribution of titanium in all forms of living and dead matter may now be regarded as settled. While no opinion is hazarded by the writer upon the rôle played by

¹ This laboratory. Work unpublished.

² See "Clay Deposits and Clay Industry in N. C." Bulletin 13, N. C. Geological Survey, by Dr. H. Ries.

³ *Vide supra*.

⁴ This Journal, 21, 706.

⁵ A true rib and clavicle.

⁶ Pectoral muscles, *latissimus dorsi* and *gluteus maximus*. I am indebted to Dr. C. S. Maugum, of this University, for kindly dissecting out these samples.

titanium in animal and vegetable growth, it is hoped that Dr. Wait's work will throw some light upon the subject. Doubtless had we as delicate and convenient tests for the other less common elements we should find their occurrence as widespread. Thus the asseverated belief of Hillebrand in the universal occurrence of all the elements in the earth's crust is extended.

Titanium was determined by Weller's well-known method as modified by W. A. Noyes, Dunnington, and Hillebrand.

UNIVERSITY OF NORTH CAROLINA.

THE RELATION OF PHYSICAL CHEMISTRY TO TECHNICAL CHEMISTRY.¹

BY WILDER D. BANCROFT.

Received October 2, 1899.

STUDENTS ask me often what use physical chemistry can be to them if they are going into technical work and, once or twice, a manufacturer has said to me that "of course, physical chemistry has no practical usefulness." It is this idea, that physical chemistry is not a necessary part of the technical chemist's equipment, which I wish to combat. Let me warn you in advance, however, not to take anything that I shall say as an argument in favor of substituting a study of physical chemistry for a study of organic or inorganic chemistry. Nothing is farther from my thoughts. A good working knowledge of inorganic and organic chemistry is absolutely essential to the man who is going to use his physical chemistry either for purely scientific purposes or for technical purposes.

To understand the usefulness of physical chemistry to the manufacturer, it is necessary to ask what the manufacturer needs. He is interested in the discovery of new and useful compounds, and in the improvement of methods for making compounds already known. The discovery of new and useful compounds may be left, for the present, to the man who is an inorganic or an organic chemist, pure and simple: it is his especial province. What I wish to emphasize is that this is, as a rule, a matter of secondary importance. There are very few manufacturers who make their profits entirely from the sale of a compound which they alone have the right to make. The

¹ Revised from a paper read before the American Chemical Society at Columbus, September 21, 1899.

American chemist makes and sells compounds which others also make and sell. He has to face competition in this country and competition from abroad. His chance of making money, apart from advantages of position, lies in the use of better methods, in getting a larger yield at the same cost or in getting the same yield at a less cost. How to do this is the problem of the manufacturer and no course of education can be considered really satisfactory which fails to take this into account.

Having found out what is needed, the next question is how to get it. To my mind, specialization and research work in organic or inorganic chemistry do not give the proper training. Let us consider for a moment what sort of training a man gets from a study of organic chemistry. Organic chemistry is at present the chemistry of new compounds. The object of a thesis in organic chemistry is to make new compounds, or to bring out more clearly the relation between two or more compounds. A man specializing in organic chemistry gets a training in manipulation and in methods of making new compounds; in addition, he increases his knowledge of chemistry and of chemical phenomena. This work qualifies him to meet one of the requirements of the manufacturer; he can make himself valuable in discovering new and useful compounds, and in working out new methods of making compounds already known. His training has not been of a nature to make himself especially valuable in improving methods. In ninety-nine cases out of a hundred, the man doing research work in organic chemistry is interested in making a reaction go, or in getting enough of any given substance to go on with. While he would rather get a ninety per cent. yield than a ten per cent. yield, he is too much interested in the substance that he is getting, or in the one that he is going to make from that, to be willing to spend much time in a possibly fruitless effort to increase the yield. By this, I do not mean to imply that the organic chemist has necessarily erred in his choice of goal; he has modern organic chemistry to show as a result. I wish to emphasize the fact that the ideals of the organic chemist are not the ideals of the manufacturer, and that a training in organic chemistry is not the best training for a technical chemist. I have laid stress on the training in organic chemistry rather than on the training in inorganic chemistry, because

organic chemistry rather overshadows inorganic chemistry in most of our universities and colleges. It is, however, equally clear that inorganic chemistry, as now taught, does not offer the ideal training for a technical chemist.

Let us now turn to physical chemistry. If organic chemistry be called the science of new compounds, physical chemistry will have to be defined as the science of methods. The physical chemist studies the reaction and not the end products. The organic chemist, or the inorganic chemist, as the case may be, tells him what the initial and final products of a reaction are, and the physical chemist then proceeds to study that reaction qualitatively and quantitatively, with special reference to such factors as initial concentration, temperature, solvent, pressure, electrical stress, and time. He does more than this. He correlates his facts and draws conclusions from them, so that it becomes possible to generalize from one reaction to all reactions. It is here that the value of physical chemistry as a training for the technical chemist comes in. It is no longer necessary to work each step of reaction out by itself. We can profit by what we have learned with regard to other, apparently dissimilar, reactions. A single instance will make clear what I mean. A certain reaction gives a fifty per cent. yield under certain conditions, and the question comes up whether changing the temperature will help matters. The man who has not studied his physical chemistry will be forced to make one experiment at a higher and one at a lower temperature in order to determine whether raising or lowering the temperature will increase the yield. If there happens to be a secondary reaction taking place, this may mask the primary reaction, and even cause false conclusions to be drawn. The man who has studied his physical chemistry finds out whether the reaction absorbs or evolves heat, and can then predict the effect of a change of temperature. If the actual result does not tally with that expected, he knows that there must be some secondary reaction taking place, and he will then proceed to minimize this. A most striking instance of this waste of money due to lack of theory is to be found in the history of the blast-furnace.

I am indebted to Dr. H. W. Wiley of the Agricultural Department for the following illustration of the practical appli-

cation of a fact that appears at first sight to have theoretical interest only. It was found recently in California, after a very dry summer, that beet-sugar could not be made in the usual way, owing to the presence of a relatively large amount of colloids in solution. Mr. E. C. Burr took advantage of the fact that colloids diffuse much less rapidly than crystalline substances, and solved the problem by shortening the time of extraction. It is evident in this case that a man with no theory to guide him might have experimented a very long time before finding the right conditions.

Even in cases where there is no theory applicable as yet, a training in physical chemistry will prove invaluable. In many industries, the color industry for instance, the physical state of a preparation is of great importance. While we cannot at present predict the conditions necessary to produce a product having the required properties, the man who has been trained to vary one factor at a time, and to note the effect of that change, will reach the goal more quickly than the inorganic or organic chemist who, quite unconsciously, allows two or more factors to vary simultaneously. If any one doubts this, let him look up the literature on the allotropic forms of the elements, or on the transformation of isomers and he will see how little attention has been paid in the past both by the inorganic and organic chemist to the conditions affecting equilibrium.

A point of great interest, technically, is the question whether a reaction will run on a large scale as well as on a small one. Many factors, such as stirring, filtration, keeping the temperature constant, etc., are often negligible in the laboratory and yet become of vital importance when the work is carried out on a large scale. Here again the training of the physical chemist should stand him in good stead. Having worked out the conditions under which the reaction goes properly, he is in a position to tell whether the disturbing factors are of such a nature as to become serious when the quantities are increased. In connection with this, I wish to call your attention to the importance of determining the conditions under which the reaction does not go as well as those under which it does go. Experimenting on a large scale is only possible to a limited extent owing to the expense involved and it should never be necessary

to fail twice in the same way. While it is not always possible to do on a large scale what can be done on a small scale, there is something wrong when a chemist cannot repeat in the laboratory the results he has obtained in the factory.

A training in physical chemistry means, or should mean, a training in methods and in the application of general principles to particular cases. A physical chemist has two advantages over another chemist when it comes to attacking a technical problem. He has had previous practice along that line, and he has his general principles or laws to guide him so that he does not need to grope aimlessly, waiting for a fortunate accident. It is thus clear that the young man who has studied physical chemistry should be more serviceable to the manufacturer than the young man who has not; but we then come face to face with the question whether we so teach physical chemistry that our students are really as superior to other students as they ought to be. I am afraid that this is not the case as yet, and that the fault lies in our teaching.

Personally, I do not believe in the teaching of technical chemistry as technical chemistry. To my mind, a comparison of German results with English results shows very conclusively that the best way to teach technical chemistry is to teach scientific chemistry. There are, however, many ways of teaching scientific chemistry and I am quite willing to admit that we do not yet teach physical chemistry in the best possible way. Physical chemistry, in its present form, is a development of the last fifteen years. Although lectures on this branch of chemistry are given at most of the universities in this country, chairs have been established only at Wisconsin and at Cornell. Under these circumstances, it will be profitable to consider, for a moment, what our shortcomings are and how they are to be remedied.

The chief criticism that I should make on all teachings of physical chemistry, including my own, is that we fail to emphasize the fact that the laws of chemistry are tools to be used rather than things to be remembered. Everyone who has worked in a laboratory appreciates the wide gulf that exists between knowing a thing and being able to use that knowledge. The ability to use knowledge comes from practice and our laboratory courses

should be extended so as to include practice in applying the general principles that have been learned. I use the word "applying" in contradistinction to the word "demonstrating" because I do not mean laboratory work supplementing the lectures. That we now have. We give our students practice in freezing-point, boiling-point, reaction velocity, conductivity determinations, etc., etc. These experiments are intended to familiarize the student with the method and the apparatus, to enable him to test the general principles, and thus to make him understand and remember them; but these experiments do not teach him how to apply the general principles in concrete cases and I think it is more than probable that a student might do all these and yet not prove himself markedly superior in technical work to a man who had not had these advantages. It seems to me that the training is bound to be incomplete unless, in addition, each man takes up some method, not necessarily a technical one, and studies that in detail, finding out how the yield can be increased, why it can be increased, and how that could have been discovered with the minimum expenditure of time. After such a drill, the student begins to appreciate that the theoretical generalizations are meant for use; he also learns what will be of immense service to him in case he goes into technical work, that it is often possible to obtain an enormously increased yield by relatively slight changes in the conditions of the experiment. We have had an instance of this at Cornell during the past year. One of my students took up the question of the electrolytic reduction of potassium chlorate and had no difficulty in increasing the efficiency from below ten per cent. to ninety per cent. and upwards. This particular reaction will never be of any technical importance because potassium chlorate is now made on a large scale by the electrolytic oxidation of potassium chloride. The training obtained by determining the effect of the different factors on the percentage yield will stand that man in good stead, no matter what problem in electrochemistry he may be called upon to solve. Another problem which has been taken up at Cornell during the past year is the question of the best method of separation by fractional distillation. Although these experiments are not yet finished we have already obtained results

which are distinctly superior to any that have been reached previously.

These two instances are cited to show the feasibility of the plan that I am advocating. There is no limit to the amount of work that can be done along this line. For instance, it would be most profitable to take any one of the little laboratory manuals in organic chemistry and work through the experiments with a view of improving the conditions. From a cursory inspection, I should say that there are very few cases in which an increased yield could not be obtained. The advantages of such a drill would be very great whether the student was going into technical work or intended to devote himself to pure science.

There is no reason, save lack of time, why the student should not be given a training in the application of general principles to methods. This lack of time will disappear as soon as teachers, students, and manufacturers appreciate the importance of such work. There is one other point in which the physical chemistry is still seriously defective. The majority of the papers on physical chemistry published every year deal with so-called dilute solutions, solutions containing less than two per cent. of one of the components. Practically all of our quantitative theory of solutions fails to apply to ninety-six per cent. and over of the possible field. We have accomplished a great deal inside the narrow limits we have set ourselves, but it is obvious that we are handicapped seriously in the application of physical chemistry to technical chemistry so long as we discuss quantitatively only such solutions as do not occur in technical work. Quite apart from the technical bearing, we can never obtain for physical chemistry its proper title as the science of chemistry until we can say that we do cover the whole field.

The whole matter can be summed up in a few words. A good training in physical chemistry is the best possible preparation for a technical chemist; but the ideal training in physical chemistry cannot be obtained until we have broken away from the shackles of 'ideal' solutions and until we have introduced laboratory work showing the application of general principles to methods.

APPARATUS FOR THE ANALYSIS OF ILLUMINATING AND FUEL GASES.

By GRO. E. THOMAS.

Received July 21, 1899.

THERE are many difficulties in the manipulation of the various forms of apparatus now employed for the analysis of illuminating and fuel gases. Much danger of loss is incurred in some methods of procedure incident to the repeated connecting and disconnecting of apparatus, while the size of others renders them inapplicable for easy transportation; also the necessity of frequent cleansing in some forms and the fragility of the material due to peculiarities of construction offer many obstacles in this line of chemical analysis. With these objectionable features in mind and with the desire to construct a piece of apparatus compact and efficient for technical work, the production of the form represented by figure 1 was undertaken, believing that there would be a demand for it.

The apparatus here described consists of a burette and leveling tube joined by rubber and capillary glass tubing with bottles, each of which is provided with a funnel. The dimensions are sixteen inches long by fifteen inches high. The burette is graduated to 100 cc., forty in whole dimensions, represented by the bulb 3, and the remainder in fifths of the same and is supplied with platinum terminals 4 and 5, about one-half inch from the top; it is connected with the leveling tube 7 by rubber tubing and is filled with water acidulated with sulphuric acid to decrease the solubility of the carbon dioxide in the water. The burette is joined to the absorbing bottles 15, 16, and 17 and the storing bottle 18 by the capillary tube *e* and the capillary T tubes 11, 12, 13, and 14 having stop-cocks 19, 20, 21, and 22 connected by rubber tubing; 14 is provided with a plug 34. The funnel tube of each bottle serves for the exit of liquid from below. Tubes 23, 24, and 25 are supplied with stop-cocks *b*, *c*, and *d*, none being required on the last tube as bottle 18 is used only for storing. Bottle 15 is filled with a solution of caustic potash; larger surface to increase the absorption is obtained by the use of glass tubes. Bottle 16 contains water saturated with bromine, while 17 holds the phosphorus covered with water, being

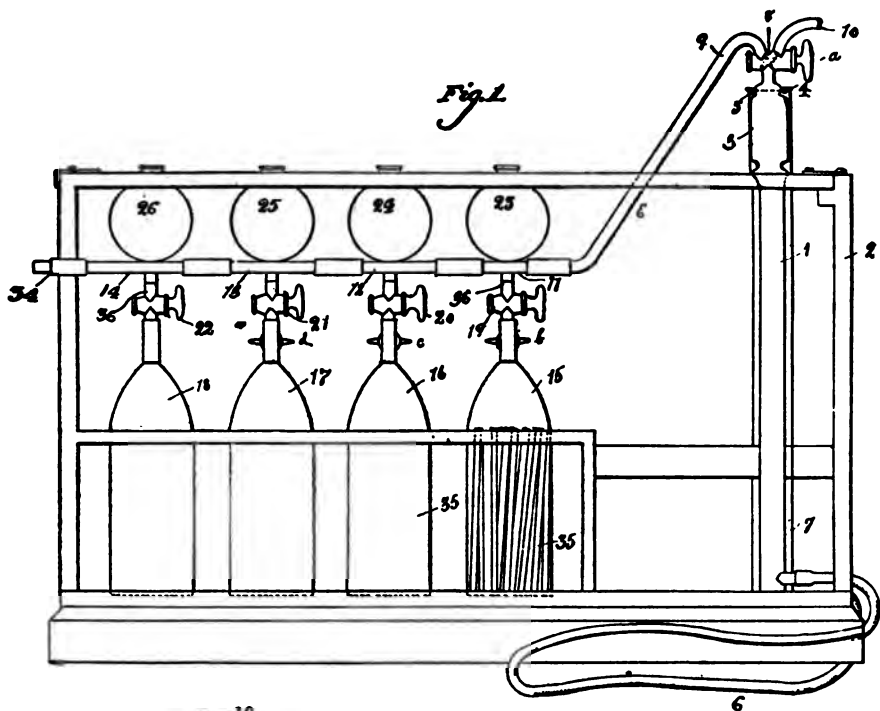


Fig. 2.

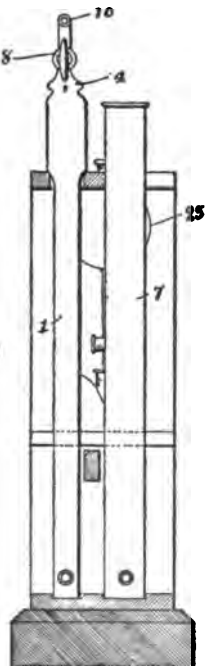
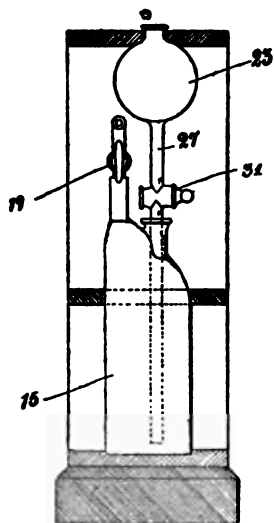


Fig. 3



protected from the action of the light by a black cloth. Bottle 18 is filled with water, as it is only used for storing gas.

Before beginning the analysis stop-cocks *b*, *c*, and *d* are opened. Upon opening the three-way cock *a* and raising the leveling tube 7, the burette is filled with water, also the capillary tube 10, which, after closing *a*, is connected with the gas supply. By lowering 7 and again opening *a*, gas is drawn into the burette; 100 cc. are measured after allowing the sides of the burette to drain. Communication is now opened between the burette and bottle 15 by means of stop-cocks *a* and 19; raising 7 forces the gas through the capillary tubing into 15. This operation is repeated three times, always allowing the water in the burette just to enter the capillary system finally bringing the solution to the mark. 19 is now closed, and the water in the burette and tube 7 is brought to the same level before closing *a*. After draining, the loss in volume is observed. The same process is carried out substantially as described for the absorption of the illuminants and oxygen by bromine and phosphorus in bottles 16 and 17 respectively, precaution being taken to completely absorb the bromine vapors in the gas after the elimination of the illuminants, by potassium hydroxide in bottle 15 and allowing the fumes to almost disappear after the absorption of the oxygen before returning the gas to the burette. Thus the carbon dioxide illuminants and oxygen are determined, after which the remainder of the gas is stored in bottle 18 prior to exploding portions with air, or air and oxygen. These direct absorptions are followed by the introduction of about 80 cc. of air into the burette through the tube 10. This is collected before the gas because of the coarser graduation in the bulb, very accurate measurement being required in this operation. By opening *a* and stop-cock 22 and lowering 7, about 15 cc. of gas are drawn into the burette. Now 22 is closed and 21 opened, thereby filling the capillary tubing to 8 with water from 17 to insure an accurate determination. Now close *a*. After draining, make a reading of the volume, and after opening communication at *a* and 19 pass the gas and air into 15 to obtain a thorough mixing, after which it is returned to the burette, the solution being brought to the mark; 19 is closed and the tubing filled as before with water from 17. Close *a* and lower 7 to reduce the

pressure. Clamp or preferably bend the rubber tubing and introduce into a slit in the side of the frame, thereby obtaining a perfect water seal, allowing no opportunities for loss when the mixture of gas and air is exploded.

Contact is now made between the platinum terminals and an induction coil attached to a battery, a spark produced therefrom igniting the mixture. A flame is seen suddenly to run down the burette, the explosion being very mild, due to the peculiarity in construction of the burette, carbon dioxide and water being the products of combustion. The gas is now allowed to assume the temperature of the room after the pressure on the tube is released. The contraction is observed, also the amount of carbon dioxide produced by absorption in 15, and the excess of oxygen in 17, the same precautions as to filling the system with water after each determination being strictly adhered to, together with the suggestion that the last time the gas is passed into 17 for the separation of the oxygen, that water from the burette be forced through the capillary system into 17 to insure complete absorption.

From the data thus obtained, it is possible to calculate the amount of hydrogen, carbon monoxide, and methane by following the well-known formulas in Sutton's "Volumetric Analysis."

(1)

$$\begin{array}{ll}
 C = 1\frac{1}{2}x + \frac{1}{2}y + 2z & x = A - D \quad C = \text{Contraction} \\
 A = x + y + z & y = \frac{3A - 2C + D}{3} \quad A = a - n = \text{Vol. of gas} - n \\
 D = y + z & z = \frac{2C - 3A + 2D}{3} \quad y = \text{Carbon monoxide} \\
 & z = \text{Methane} \\
 & x = \text{Hydrogen} \\
 & D = \text{Carbon dioxide} \\
 & n = \text{Nitrogen.}
 \end{array}$$

(2)

$$\begin{array}{ll}
 B = \frac{1}{2}x + \frac{1}{2}y + 2z & B = \text{Oxygen consumed} \\
 x = A - D & A = a - n = \text{Volume of gas} - n \\
 y = \frac{3D - 2B + A}{3} & n = \text{Nitrogen} \\
 z = \frac{2B - A}{3} & D = \text{Carbon dioxide.}
 \end{array}$$

As the excess of oxygen after the combustion is absorbed by phosphorus in bottle 17 an explosion with hydrogen is avoided. What remains after this process is completed is the nitrogen in the air plus the nitrogen in the gas; a direct determination of the latter is thus made possible.

If it should be desired to employ this apparatus for fuel gas analysis, bottles 17 and 18 can be filled with a cuprous chloride solution, using a layer of petroleum in the funnels to prevent the air having an oxidizing action upon the copper solutions. By the use of two solutions a more accurate determination is made as it is well known that one cuprous chloride solution repeatedly used is not a satisfactory reagent for the absorption of carbon monoxide. It has been found that a lubricant is absolutely essential for success with this as with similar forms of apparatus. The one mentioned in this Journal, 20, 678, is recommended but for the bottle containing bromine, vaseline is better adapted. A uniform temperature should be maintained in the laboratory as the burette is not water-jacketed. The apparatus described appears to have many advantageous features beside its compactness, which is certainly desirable, for ample space is allowed above the funnels for an induction coil and small battery, making the complete outfit to go in a case sixteen by seventeen inches. The J tubes being separate and 36 having a plug, 34 affords opportunity for rapid and easy cleansing of the capillary system. After the gas is once collected, there is no possibility of loss as it remains in the apparatus until the analysis is complete and, if necessary, several confirmatory explosions are made. All the parts are readily disconnected and sections when broken can be easily replaced. With the exception of 17, disconnection is only required in case of accident, as the other bottles may be replenished by forcing the liquids into the funnels, siphoning off and fresh solutions added. Direct explosion in the measuring burette is an advantage as it eliminates the necessity of an extra bottle for that purpose. Less than an hour is required for the completion of an analysis by this method and the results obtained have been eminently satisfactory.

THE DETERMINATION OF GRAPHITIC CARBON IN CAST AND PIG IRON.

BY ALLEN P. FORD AND I. M. BREGOWSKY.

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GRAPHITIC carbon in cast iron is usually determined by dissolving the iron in dilute nitric acid and estimating the residual graphite by combustion, either by the wet or the dry-method; or by drying and weighing direct on weighed paper filters, burning off the graphite and paper and subtracting the weight of the ash and silicon.

The combustion method, while generally considered to be the most accurate, requires considerable time, great care, and close attention, and even then failures are common. For these reasons it is not well adapted to the requirements of a laboratory in connection with foundries and manufacturing plants, where time is an important consideration. In these cases the weighed paper method is generally resorted to, though, in a less measure, it is open to the same objections as the combustion method. Aside from the time required for two dryings in the air-bath of an hour to an hour and a half each, and three weights with time for cooling each time, one must take care that the paper is thoroughly dried without being charred and that no loss occurs in the transfers of the filter-paper from funnel to weighing-bottle and back again.

Under the conditions there appeared to be no reason why the graphite could not be filtered, burned off and determined by direct loss on a Gooch. At first, in order to make the experiment inexpensive, a porcelain Gooch was used, but it was found to be very difficult to get sufficient heat through the thick and comparatively clumsy porcelain crucible to burn off all the graphite. Furthermore, when the attempt was made to ignite the crucible and freshly prepared asbestos felt previous to filtering the graphite, the bottom of the crucible usually broke off. Being convinced that the method was practicable, however, a platinum Gooch was obtained and this difficulty overcome.

Then much annoyance was experienced in filtering. When the iron contained much silicon, enough would separate with the graphite to clog the asbestos felt, and hinder the filtration, sometimes even making it impossible. As hydrofluoric acid had

been used to eliminate the silicon in the determination of manganese, it was tried for the same purpose in the graphite. The result was very satisfactory.

The silicon was disposed of, and the filtration made easy and rapid. Also many determinations can be made on the same asbestos felt while in the first case only one could be made without changing the felt. It remained to be ascertained whether the hydrofluoric acid had any effect on the accuracy of the result in any way.

To determine this point a number of analyses were made in pairs, in one case with hydrofluoric acid and in the other without. The results checked closely and proved that the hydrofluoric acid did not affect the accuracy of the method.

Determinations by this method with and without hydrofluoric acid were also checked with duplicate samples by the paper method. The results agreed closely. In fact, in some cases where a number of determinations were made on one sample, those by the Gooch showed more uniformity than those by weighed papers. This was attributed to the fact that the weight of the paper may vary before and after filtering. The details of the method are as follows :

One gram of pig or cast iron is dissolved in nitric acid (sp. gr. 1.12), better without boiling. When solution is complete, or nearly so, a few drops of hydrofluoric acid are added, more or less according to the amount of silicon present, and boiled a short time.

This boiling will drive off the hydrofluoric acid or nearly so, and insure complete solution of the iron. The acid solution is then diluted with four or five times its volume of water and filtered by slight suction on a Gooch.

Care should be taken in the selection of asbestos for this purpose. It should be digested in hydrochloric acid and, in case of a freshly prepared felt, it should be ignited until there is no further loss of weight, before the graphite is thrown on it.

After the first determination it is only necessary to wash it each time. This is advisable as each ignition has a tendency to open up the felt, and the washing under suction settles the asbestos down in place and makes as good a filtering medium as in the first determination.

It also washes out any fine particles of asbestos which might possibly be lost in the subsequent ignition. After washing with hot dilute hydrochloric acid and hot water, the crucible with contents is dried an hour or an hour and a half at 120° , the length of time it is dried depending somewhat on the amount of graphite.

The crucible is then cooled, weighed, the graphite burned off, and the crucible cooled and weighed again, the difference between the two weights being the graphite.

The advantages of the method are, a very considerable saving of time, less liability to error by doing away with the paper filter, and the avoidance of the necessity of such close attention since a variation in the temperature of the air-bath that would be fatal to a paper filter will not affect the graphite. Also, in the absence of the paper, the air-bath can be run at a much higher temperature, thus making the thorough drying of the graphite certain.

A few experiments were made with samples containing about three per cent. of graphite to determine the loss by boiling in nitric acid.

It was found that when using nitric acid (sp. gr. 1.20) and boiling from one to three hours, there was a loss of from 0.16 per cent. to 0.32 per cent. In using nitric acid (sp. gr. 1.12), however, the graphite was apparently not affected when boiled one hour after the iron was dissolved and the solution ready to filter.

In some cases there was a loss of a few hundredths of a per cent. and in others a slight gain. In all cases, however, the difference was within the limit of the legitimate error of manipulation and simply showed that there was no oxidation of the carbon by the nitric acid.

From these experiments it was pretty clearly demonstrated that there is no loss of graphite when using nitric acid (sp. gr. 1.12), even if the boiling is continued much longer than necessary.

REPORT OF THE COMMITTEE ON COAL ANALYSIS.

To the President and Members of the American Chemical Society:

SOME time ago a preliminary report of this committee was presented to the society.¹ The committee desire, now, to present the following as their final report. In doing this, they are well aware that more experimental work on some points in the report is very desirable. But no member of the committee is able, at present, to give much further time to the matter and it is felt that nothing can be gained by further delaying the report.

In presenting the report the committee wish to express their thanks to those who have so kindly aided the committee by their criticisms and otherwise; especially to Mr. W. H. Clingerman, of the Frick Coke Co., who furnished samples of the Pennsylvania coking coals; to Mr. R. C. Hills, of the Colorado Fuel and Iron Co., of Denver; to Mr. William Kent, of the *Engineering News*; to Mr. William Glenn, of the Baltimore Chrome Works; to Professor N. W. Lord, of Ohio State University, Columbus; to Mr. G. L. Heath, of the Calumet and Hecla Smelting Works, South Lake Linden, Mich; to Mr. Geo. H. Eldridge, of the U. S. Geological Survey; and to Messrs. R. W. Atkinson and A. J. Atkinson, of Cardiff, Wales.

METHODS OF ANALYSIS.

1. *Sampling*.—In sampling from cars proceed as follows: Beginning at one corner of the car, drive a scoop-shovel vertically down as deep as it will reach. Bring it out with all the coal it will hold and throw into a cart or wheelbarrow. Repeat, taking six scoopfuls along one side of the car, at equal intervals, six through the center and six along the other side. Place the coal taken on a close, tight floor. Break all lumps larger than an orange. Mix by shoveling it over on itself, back and forth. Quarter, and reject opposite quarters. Break finer, as may be necessary, and continue to quarter down till a sample is obtained small enough to go into a quart fruit jar and having no pieces larger than one-fourth inch cube. The sample may, with advantage, be run rapidly through a mill which will break it to

¹ This Journal, 20, 281.

the size mentioned. Transfer to the jar and make sure the latter is sealed air-tight before it is set aside. All of these operations should be conducted as rapidly as possible to guard against any change in the moisture content of the coal.

Modifications of this method of sampling will, of course, suggest themselves, and in some cases will be necessary. When possible, a more representative sample may be secured by taking shovelfuls of the coal at regular intervals during the loading or unloading of the car. In any method of sampling, two conditions must be insisted on; the original sample should be of considerable size and thoroughly representative, and the quartering down to an amount which can be put in a sealed jar should be carried out as quickly as possible after the sample is taken. Unless the coal contains less than two per cent. of moisture, the shipment of large samples in wooden boxes should be avoided.

In boiler tests, shovelfuls of coal should be taken at regular intervals and put in a *tight, covered* barrel, or some air-tight covered receptacle, and the latter should be placed where it is protected from the heat of the furnace.

In sampling from a mine, the map of the mine should be carefully examined and points for sampling located in such a manner as to fairly represent the body of the coal. These points should be placed close up to the advancing crescent-shaped front of the workings. Before sampling, make a fresh cut of the face from top to bottom to a depth which will insure the absence of possible changes or of sulphur and smoke from the blasting-powders. Clean the floor and spread a piece of canvas to catch the cuttings. Then, with a chisel, make a cutting from floor to roof, say three inches wide and about one inch deep. Do not chisel out the shale or other impurities that it is the practice at that mine to reject. Measure the length of the cutting made but do not include the impurities in this measurement. With a piece of flat iron and hammer break all pieces to quarter inch cube or less, without removing from the cloth. Quarter down and transfer to a sealed bottle or jar. For the "run-of-mine" sample, samples taken at several points in this manner should be mixed and quartered down. If the vein varies in thickness at different points, the samples taken at each point should correspond in amount to the thickness of the vein. For instance, a small

measure may be filled as many times with the coal of the sample as the vein is feet in thickness. Should there appear differences in the nature of the coal, it will be more satisfactory to take, in addition to the general sample, samples of such portions of the vein as may display these differences.

For analysis quarter down further to about 100 grams. Run this portion through a mill which admits of quick grinding with little exposure to the air. A coffee-mill set to grind as finely as possible will answer. The grinding of 100 grams is recommended because less water will be lost than if a smaller sample is ground.

When an accurate determination of moisture is required and especially with coals high in moisture a portion of this coarsely ground sample must be transferred at once to a tightly stoppered tube for use in determining moisture.

Grind twelve to fifteen grams of the remainder moderately fine in a porcelain or iron mortar and transfer to a tightly corked tube for use in other determinations than that of moisture.

The committee wish to urge very strongly upon chemists and engineers the importance of careful sampling and of *careful treatment of the samples* in order to secure reliable results, especially in the determination of moisture.

That other factors must also be taken into consideration, in some cases, is illustrated by the following occurrence, cited by Mr. R. C. Hills.

"A railway manager had a car of coal from the South Platte field sampled and got me to analyze it. The sample was taken in the summer time and although a lignite, containing, usually, twelve per cent. of moisture, it only afforded ten per cent. Later on he concluded to try a car from the Franceville field, also lignite, affording in the summer time about fifteen per cent. of moisture. The sampling was done in the latter part of November and I obtained about twenty-one per cent. out of it. In both cases determinations were made elsewhere. The result was great injustice to the Franceville operators and to the best interests of the railway. Evidently there was accordance between the chemists on each sample but had the conditions under which the samples were taken been reversed each would have varied several units from the values found."

A car-load of many western coals may lose several hundred

pounds of moisture daily while standing on the track and the same coal may lose several per cent. of moisture by standing for a few days or weeks in a loosely stoppered bottle.

2. *Moisture*.—Dry one gram of the coal in an open porcelain or platinum crucible at 104° – 107° for one hour, best in a double-walled bath containing pure toluene.¹ Cool in a desiccator and weigh covered.

With coals high in moisture, and in all cases where accuracy is desired, determinations must be made both with the coarsely ground and with the powdered coal. When, as will usually be the case, more moisture is found in the coarsely ground than in the powdered coal, a correction must be applied to all determinations made with the latter. Thus, if one per cent. more of moisture is found in the coarsely ground sample a total of one per cent. must be subtracted from the quantities of the other constituents as determined with the powdered sample. Or, in the form of a rule: Divide the difference in moisture by the per cent. of other constituents than moisture as found in the powdered coal. Multiply the per cent. of each constituent as found in the powdered coal by the quotient and subtract the resulting product from the amount of the given constituent.

Thus, suppose the results of an analysis give:

	Coarsely ground coal.	Powdered coal.
Moisture	12.07	10.39
Volatile combustible matter	34.25

then the correction factor will be

$$\frac{12.07 - 10.39}{100 - 10.39} = \frac{1.68}{89.61} = 0.0187$$

and the true per cent. of volatile combustible matter will be

$$34.25 - (34.25 \times 0.0187) = 33.61.$$

It is possible that volatile combustible matter and ash may be determined with the coarsely ground coal without serious error but we have not enough data at our command to warrant such a recommendation.

The toluene bath is recommended for convenience, but any other bath at the proper temperature will answer equally well. In all cases recorded below, the coals gained in weight, probably

¹ Victor Meyer: *Ber. d. chem. Ges.*, 17, 2999.

from oxidation, after one hour's heating, so that longer heating is not only unnecessary but undesirable. A higher temperature appears also to be undesirable (see below).

The results of Dr. Hillebrand as to the loss of moisture *in vacuo* over sulphuric acid, recorded in our first report, have been confirmed by the following results obtained by Mr. N. M. Austin at the Rose Polytechnic Institute. The results are in most cases, averages of from two to six determinations.

No.	Toluene. First hour. 107° C.	Toluene. Second hour. 107° C.	Xylene. First hour. 138° C.	Xylene. Second hour. 138° C.	In vacuo over sulphuric acid. Seven hours.	In vacuo over sulphuric acid. Twenty-four hours.	In vacuo over sulphuric acid. Sixty-four hours.
1	0.97	0.92	1.03	0.98	1.17	∴ ∴ ∴	1.18
2	4.55	4.61	4.60	4.56	4.69	5.05
3	1.39	1.27	1.27	1.15	1.46	1.45	1.56
4	1.31	1.29	1.27	1.20	1.36	1.38	1.39
5	1.00	0.97	0.97	0.96	1.10	1.14
6	1.44	1.31	1.22	1.15	1.46	1.49	1.56
7	14.53	14.23	14.85	14.28	14.91	15.47	15.25
8	8.43	8.21	8.31	8.22	8.91	8.90	8.95
9	1.34	1.32	1.23
10	10.50	11.04	11.55

While it is evident that more water, and doubtless, more nearly the amount of water actually present, can be obtained by drying for twenty-four hours *in vacuo* over sulphuric acid than by drying for one hour at 104°-107°, the committee are not prepared to recommend so radical a departure from common usage for general adoption. They believe that drying *in vacuo* should be used when great accuracy is desired and in all cases where the determination is to be combined with an ultimate analysis, but that so long as the conditions of sampling are not more carefully controlled than at present, the difference between the two methods (average 0.37 per cent.) is not great enough to justify the general adoption of the new method.

The small difference found between the determinations at 107° and those at 138° (0.03 per cent. more at the lower temperature on the average) indicates that a variation of several degrees in the temperature of the bath will have no appreciable effect on the determination, provided the temperature is above the boiling-point of water.

A series of comparative determinations made in porcelain and platinum crucibles gave slightly higher values, on the average 0.12 per cent., in the porcelain. This was probably due to the greater depth of the platinum crucibles, causing the moisture to diffuse away more slowly.

For coals containing less than two per cent. of moisture, satisfactory results can be obtained by drying for twenty-four hours in a watch-glass over sulphuric acid, at atmospheric pressure (C. B. Dudley). For lignites, and for coals containing a high per cent. of moisture, the method is not satisfactory.

The following determinations made by the chairman of the committee demonstrate the impossibility, under some laboratory conditions, of grinding coal in a mortar without serious loss of moisture. In these determinations about 100 grams of the coal were ground in a coffee-mill and then ten to twenty grams of this coarsely ground coal were ground as quickly as possible in an iron mortar and transferred at once to a stoppered tube.

No.	Temperature of laboratory.	Ground once in a coffee-mill.		Ground twice in a coffee-mill.		Ground in an iron mortar.
		16 to 20 grams, one hour at 135°.	1 gram, one hour at 107°.	16 to 20 grams, one hour at 135°.	1 gram, one hour at 107°.	1 gram, one hour at 107°.
1	88° F	{ 12.07 12.14	11.70	{ 10.39 11.09
1	76° F	11.96	11.92	11.43
2	88° F	12.32	11.05
3	77° F	13.61	13.85	13.38	13.67	12.83
3	66° F	13.92	14.06	13.56	13.72	13.24
4	78° F	1.33	1.22	1.33	1.16	1.03

Coal No. 3 gave *in vacuo* over sulphuric acid for twenty-four hours:

	Per cent.
Ground once	14.03
Ground twice	13.88
Ground in mortar	13.62

Coal No. 4 gave on further drying *in vacuo* for twenty-four hours after heating for one hour at 107°:

	Per cent.
Ground once	1.26
Ground twice	1.24
Ground in mortar	1.07

A large amount of additional work on the subject of moisture, with coals of a greater variety, seems desirable. Enough has been done, however, to demonstrate that a close approximation to the truth can be obtained only by the most careful treatment of the samples. Every coal analyst, who has not given careful attention to the question, should convince himself by comparative determinations that the methods which he uses do not cause serious loss of water before the determination is made.

Volatile Combustible Matter.—Place one gram of fresh, undried, powdered coal in a platinum crucible, weighing twenty or thirty grams and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom six to eight cm. above the top of the burner. The flame should be fully twenty cm. high when burning free, and the determination should be made in a place free from draughts. The upper surface of the cover should burn clear but the under surface should remain covered with carbon. To find "Volatile Combustible Matter" subtract the per cent. of moisture from the loss found here.

The method recommended in our first report, and given here without change, has been the occasion of considerable discussion within the committee, and also by others. Very little experimental evidence has been submitted to us, however, and that obtained by Mr. Austin at the Rose Polytechnic Institute appears to be decidedly in favor of the method given (see below).

The method differs from that of Muck¹ in placing the crucible six to eight cm. above the burner instead of three cm. and in continuing the heating for a definite length of time. The flame is much hotter at six to eight cm. above the burner than at three cm., and, if the full flame is used, as directed, the crucible will be sufficiently well covered by it. The time limit corresponds more nearly to present practice in America and is likely to give more concordant results than Muck's direction to stop heating with the disappearance of flame at the edge of the lid of the crucible. The time limit is that proposed by Hinrichs, but the use of a blast is omitted.

In discussing the subject, it should be distinctly understood,

¹ *Chemie der Steinkohle*, p. 10.

at the outset, that the term "Volatile Combustible Matter" does not represent any definite compound or class of compounds which exist in the coal before heating. Mr. Austin's results demonstrate that some of the carbon which escapes in the form of volatile compounds on rapid heating, is separated in the free state and remains as "Fixed Carbon" when the first heat is applied slowly. It is well known, too, that many of the compounds contained in the gas and tar formed by heating bituminous coals are decomposed by heat with the formation of free carbon. The "Fixed Carbon" retains a considerable amount of hydrogen which is progressively expelled by heating to higher and higher temperatures, until, at temperatures approaching that of the electric arc, it all escapes and the carbon remaining crystallizes in the form of graphite. It follows, therefore, that, no matter what method of heating, or what temperatures are used, the determination must be an arbitrary one.

The two considerations which should have greatest weight in the selection of a method appear to be that the method chosen should, if possible, give results which approximate closely to those obtained in the commercial manufacture of coke from the same coals, and that the method should be one which can be accurately described so that different operators will secure concordant results with samples of the same coal. No experimental evidence on either point has been furnished the committee. Some evidence upon the first point is furnished by Mr. Austin's work below, and the results are certainly favorable to the method which we propose.

The most serious objection which has been raised against the method is the claim that certain non-coking coals suffer mechanical loss from the rapid heating. No evidence as to the extent of such loss has been given. The following determinations of ash in the original coal, and in the coke obtained by the method recommended, prove that in the case of these coals, at least, any mechanical loss which occurred must have been insignificant. Coals 5, 6, 7, and 8 were coking coals; 10 was a non-coking coal from Colorado.

	Ash from coal.	Ash from coke.
5	{ 4.74 4.73	4.75
6	{ 5.43 5.35 5.39	5.43
7	{ 2.32 2.37	2.32
8	13.52	13.52
10	10.62	10.60

Further determinations of this kind with non-coking coals are very desirable, but, even if a small amount of mechanical loss is found to occur in such cases, it does not follow that a different method should be used for them. Since the determination is, in any case, an empirical one, uniformity in the method for all cases is extremely desirable.

One chemist has furnished us with data which show that he has obtained, with the use of a Rose crucible in a muffle, results which agree closely with those obtained by the method proposed by the committee. Further evidence upon this point is very much desired, as the exigencies of many laboratories demand that the determinations should be made in a muffle.

The following determinations of coke by different methods were made by Mr. N. M. Austin. The coals used were:

3. Coking coal, Leith Mine, Pa.
4. Coking coal, Mammoth Mine, Pa.
5. Coking coal, McClure Mine, Lemont, N. Y.
6. Coking coal, Valley Mines, Pa.
7. Lancaster semiblock coal, Owen Co., Indiana.
8. Coking coal used at the Terre Haute Water Works.
9. Coking coal from Hantana, Tennessee.
10. Non-coking coal from Colorado.

Coals 3, 4, 5, and 6 were furnished by Mr. Clingerman of the Frick Coal Co., with the statement that these coals run very evenly for the production of coke, and give a yield of sixty-eight to seventy per cent.

No.	Seven minutes, full flame. Wet coal.	Seven minutes, full flame. Dry coal.	Five minutes, inch high flame. Five minutes, full flame.	Three and a half minutes, full flame. Three and a half minutes, over blast.
3	{ 67.33 67.36	{ 67.03 67.50 67.62 67.96	71.55	66.52
4	{ 68.96 69.02	68.92	73.41	67.92
5	{ 68.55 68.31	67.78	72.88	67.71
6	{ 68.97 68.90	68.99	{ 73.60 72.92	67.41
7	{ 48.82 49.27	{ 50.30 50.46	54.32	46.91
8	{ 53.70 53.65	53.57	59.00	51.58
9	{ 65.68 65.94	65.75	70.30	65.35
10	41.48	{ 41.55 37.40	45.43	39.31

The moisture in these coals is given on p. 1120. The agreement with the commercial coking value for the Pennsylvania coals must be considered as satisfactory. The effect of slow heating in increasing the amount of coke is very evident. The amount of coke, or of fixed carbon, by slow heating was, on the average, 4.58 per cent. higher than by the rapid heating. That this is not due to mechanical loss is proved by the ash determinations above.

In using the blast, the flame of the blast was applied before the flame of the Bunsen burner was removed. The results are, on the average, 1.38 per cent. lower than with the Bunsen alone. It is believed that this is not due entirely to the expulsion of volatile matter, but, in part, to the fact that the flame of the blast is more strongly oxidizing and carbon dioxide and water-vapor enter the crucible from it in larger amount. The fact that the western coals, 7, 8, and 10, with their more porous, and, in the last case, pulverulent coke, show much greater differences than the others, supports this view. The results with the Bunsen alone approach more nearly to the commercial coking values, and it is believed, too, that they are much more likely to give concordant results in the hands of different operators.

Little difference is shown in the average between the results with the original wet coal and with the dry coal. The use of the wet coal is recommended because the drying causes changes in the coal otherwise than by expelling the moisture, and because undried coal is always used in the manufacture of coke. No time is lost by such a procedure, since the ash can be determined much more quickly with the coal used for the moisture determination than with the coke. It took four hours to burn the coke to ash in a platinum crucible, while the dry coal may be burned in a porcelain crucible in two hours or less.

The results of Messrs. Meade and Attix published in this Journal (21, 1137) seem to show very clearly that the heating of coke or anthracite coal in a crucible with the blast, causes a very considerable loss by oxidation. It is probable that heating with the blast in an atmosphere of nitrogen or hydrogen is the most satisfactory method for materials of this class, but further comparisons of the results obtained in that way with the results obtained by the method recommended by the committee are very desirable.

Ash.—Burn the portion of powdered coal used for the determination of moisture, at first over a very low flame, with the crucible open and inclined, till free from carbon. If properly treated, this sample can be burned much more quickly than the dense carbon left from the determination of volatile matter. It is advisable to examine the ash for unburned carbon by moistening it with alcohol.

When the sulphur in the coal is in the form of pyrites, that compound is converted almost entirely into ferric oxide in the determination of ash, and, since three atoms of oxygen replace four atoms of sulphur, the weight of the ash is less than the weight of the mineral matter in the coal by five-eighths of the weight of the sulphur. While the error from this source is sometimes considerable, the committee does not recommend such a correction for "proximate" analyses. When analyses are to be used as a basis for calculating the heating effect of the coal a correction should be made (see below).

5. *Fixed Carbon.*—This is found by subtracting the per cent. of ash from the per cent. of coke as found in paragraph 3. Sulphur, which passes partly into the "Volatile Combustible

Matter'' and partly into the coke, is not considered in the calculation.

6. *Sulphur*.—Eschka's method is recommended for general use. The following directions, which are given for the convenience of those using this report, are those of G. L. Heath¹ with slight modifications.

Mix thoroughly, one gram of the finely powdered coal² with one gram of magnesium oxide and one-half gram of dry sodium carbonate, in a thin platinum dish having a capacity of 75 to 100 cc. A crucible may be used but a dish is preferred. The magnesium oxide should be light and porous, not a compact, heavy variety.

The dish is heated on a triangle over an alcohol lamp, held in the hand at first. *Gas must not be used*, because of the sulphur it contains. The mixture is frequently stirred with a platinum wire and the heat raised very slowly, especially with soft coals. The flame is kept in motion and barely touching the dish, at first, till strong glowing has ceased, and is then increased gradually till, in fifteen minutes, the bottom of the dish is at a low, red heat. When the carbon is burned, transfer the mass to a beaker and rinse the dish, using about fifty cc. of water. Add fifteen cc. of saturated bromine water and boil for five minutes. Allow to settle, decant through a filter, boil a second and third time with thirty cc. of water, and wash till the filtrate gives only a slight opalescence with silver nitrate and nitric acid. The volume of the filtrate should be about 200 cc. Add one and a half cc. of concentrated hydrochloric acid, or a corresponding amount of dilute acid (eight cc. of an acid of eight per cent). Boil till the bromine is expelled and add to the hot solution, drop by drop, especially at first, and with constant stirring, ten cc. of a ten per cent. solution of barium chloride. Digest on the water-bath, or over a low flame, with occasional stirring till the precipitate settles clear quickly. Filter and wash, using either a Gooch crucible or a paper filter. The latter may be ignited moist in a platinum crucible, using a low flame till the carbon is burned.

In the case of coals containing much pyrites or calcium

¹ This Journal, 20, 630.

² With coals high in moisture a correction may be necessary on account of the loss of water in powdering the coal. (See above under moisture.)

sulphate, the residue of magnesium oxide should be dissolved in hydrochloric acid and the solution tested for sulphuric acid.

If desirable, the burning of the coal with Eschka's mixture may be carried out in a muffle, from twenty to thirty minutes being required.¹

The following determinations made by Geo. Steiger, under the direction of Dr. Hillebrand, demonstrate the necessity of examining the residue of magnesium oxide and ash for sulphur. In these determinations both ammonium nitrate and bromine water were used.

	Sulphur extracted by water.	Additional sulphur ex- tracted by hydrochloric acid.	Total sulphur.
1	4.447	0.114	4.561
2	0.744	0.057	0.801
3	0.613	0.037	0.650
4	1.888	0.111	1.999
5	2.652	0.067	2.719
6	1.392	0.082	1.472
7	1.879	0.083	1.962
8	0.957	0.041	0.998
9	0.593	0.032	0.625

A mixture of five grams of the sodium carbonate and ten grams of the magnesium oxide should be boiled several times with water, the solution filtered and acidified, the amount of sulphuric acid present, if any, determined, and the appropriate correction applied. The operator should, of course, satisfy himself that the bromine water and hydrochloric acid used are free from sulphur.

The following method of R. W. and A. J. Atkinson deserves consideration from those who find it more convenient to work in a muffle. The method has also been applied to iron ores.²

One gram of the finely ground coal or coke is mixed thoroughly with five grams of dry sodium carbonate, spread evenly over the bottom of a flat or shallow platinum dish, and the latter placed on a rectangular rest made of clay-pipe stems inside of a muffle which, though hot, is still black. The temperature of the muffle should be raised gradually during half an hour to clear cherry-redness and then kept at the latter temperature for ten or fifteen minutes. The sodium carbonate should not sinter or fuse.

¹ Rothe: *Stahl und Eisen*, XII, 31 (1894).

² *J. Soc. Chem. Ind.*, March 29, 1886; *J. Iron and Steel Inst.*, No. 2 (1896).

The mass should not be stirred. When the carbon is burned, usually in about forty-five minutes in all, cool, digest with 100-120 cc. of warm water, allow to settle, decant through a filter and wash twice by decantation and then on the filter, adding a few drops of a solution of pure sodium chloride, if the residue tends to pass through the filter. The filtrate is acidified with twelve cc. of concentrated hydrochloric acid and precipitated with barium chloride as above. No oxidizing agent is required.

R. W. Atkinson has demonstrated that the evaporation with hydrochloric acid to remove silica, which some recommend, is unnecessary. His statement is confirmed by the experience of one of the members of the committee in similar cases.

A few determinations made by this method under the direction of one of the members of the committee have given good results, but no careful examination of the method has been made.

7. *Ultimate Analysis*.—It seems to be unnecessary to give directions for the determination of carbon, hydrogen, and nitrogen here. In determining carbon and hydrogen, lead chromate or some other means for retaining sulphur must, of course, be used. The amount of nitrogen is so small that the use of a copper spiral is not necessary.

The method to be used in calculating the oxygen of the coal presents, perhaps, the question of greatest difficulty. If we could be sure that all of the sulphur is present in the form of pyrites, and that this is converted into ferric oxide in the ash, the oxygen should be found by subtracting from 100, the sum of carbon, hydrogen, nitrogen, ash and *five-eighths* of the sulphur. This is probably the safest rule which can be given for general use, and especially for coals high in sulphur. The operator should, however, satisfy himself as to whether the ash is practically free from sulphates, and, if possible, whether the sulphur is mainly in the form of pyrites. If necessary, the rule should be modified, in particular cases, accordingly.

8. *Heating Effect*.—In the preliminary report the recommendation was made that the heating effect be given on the basis of the coal burned to vapor of water at 100° C. After some criticism from others and further consideration, we have concluded to recommend that results be given for the coal burned

to liquid water at the ordinary temperature. The reasons for this recommendation are that this appears to be the common practice in this country, and because coals are burned to liquid water in the bomb calorimeter, which undoubtedly furnishes the best determinations of heating effect at present available. Engineers and others will, of course, understand that the heating effect, when stated in this manner, includes three and a half to four per cent. of heat which can never be secured under the conditions of practical use.

The most reliable formula for the calculation of the heating effect of a coal burned to liquid water is that of Dulong, which gives the calorific power in calories per kilogram.

$$\text{Calorific power} = 8080C + 34,460(H - \frac{1}{8}O) + 2250S.$$

For the calculation of the oxygen, see the paragraph on ultimate analysis.

The calorific power in British Thermal Units per pound may be found by multiplying that in calories per kilogram by nine-fifths.

The theoretical evaporative effect is to be calculated by dividing the number of calories per kilogram by 536, or the number of British Thermal Units per pound by 965, and subtracting from the result one-seventh more than the amount of water formed by burning one kilogram of the coal. The addition of one-seventh is given because the liquid water, on the basis of which the heating effect is given, must be considered as changed from water at ordinary temperature to steam at 100° C. The amount to be subtracted may be taken as 0.55 for most bituminous coals. The result gives the theoretical number of kilograms, or pounds, of water converted into steam from, and at, 100° C by one kilogram, or pound, of coal.

The rule given, tentatively, in our preliminary report for the calculation of heating effect, from the amount of combustible matter present in bituminous coals, has been found to be of limited application.

The following averages for the heating effect of the combustible matter of a series of bituminous coals, and for the composition of the combustible matter which they contain, have been calculated from the results obtained by Professor N. W.

Lord and Mr. F. Haas¹ with a bomb calorimeter. The combustible matter for the calculations included carbon, hydrogen, nitrogen, and oxygen. The oxygen was calculated on the supposition that the sulphur was present in the form of pyrites. (See paragraph 7.) The calorimeter result was corrected by subtracting the heating effect of the sulphur. The sulphur averages are given, though it was not included in the combustible matter. The results are for the coals burned to liquid water.

No of samples.	S.	C.	H.	O.	N.	Calories per kilo-gram by bomb calorimeter.	Calories per kilo-gram, calculated.
3	1.59	80.63	5.40	12.26	1.71	7860	7847
2	3.01	82.15	5.36	10.97	1.53	8148	8012
9	2.20	83.66	5.51	9.33	1.51	8255	8255
15	2.29	83.97	5.60	8.79	1.66	8372	8335
2	1.28	85.93	5.47	7.06	1.54	8508	8523
3	0.59	91.28	4.52	3.29	0.91	8783	8792

The agreement between the calorimeter results and those calculated by the formula indicates that the latter are sufficiently accurate for most purposes, when calorimeters are not available.

Professor Lord concludes from his work² that the heating effect of the combustible matter of coal from the same seam over wide areas, is nearly identical. If the heating effect has been determined for several samples of the coal a factor similar to those in the last two columns above may be calculated and this may be used with a good degree of accuracy for the calculation of the heating effect of other samples from the same seam. For the purpose of such calculations it is recommended that the combustible matter of the coal be calculated by subtracting from 100 the per cents. of ash and moisture and one half of the sulphur. If the sulphur were all in the form of pyrites five-eighths of the sulphur should be subtracted but the rule given is considered sufficiently accurate for the purpose in question.

In a similar manner, if the percentage composition of the combustible matter in a seam of coal has been determined, this

¹ Trans. A. I. M. E., 27, 259.

² Loc. cit.

may be made the basis for the calculation of a factor which can be applied for the calculation of the heating effect of other samples from the same seam.

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LEMON FLAVORING EXTRACT AND ITS SUBSTITUTES.

BY A. S. MITCHELL.

Received September 18, 1899.

AS many valuable papers have lately appeared upon the subject of vanilla flavoring extract, while little has been done upon lemon extract and its substitutes, I have ventured to here outline the results of the investigation of these goods as found upon the market, and made in the course of work for the Wisconsin Dairy and Food Commission.

Lemon extracts, following the U. S. P. formula for "Spiritus Limonis" should contain at least five per cent of oil of lemon dissolved in deodorized alcohol and should be colored only with the coloring from lemon peel.

A preliminary examination of the extracts supplied by grocers showed them to contain alcohol in amounts varying from fourteen to ninety-four per cent. by weight and oil of lemon from none to eight per cent.

The extracts low in alcohol had in many cases a fine aroma derived from agitation with new oil of lemon in some cases but more frequently produced by citral and the so-called "soluble oil of lemon" or from lemon-grass or citronella aldehyde and frequently with the addition of tincture of nutmeg, mace, or capsicum. The cheaper grades contained so little oil in solution that the addition of water frequently failed to produce turbidity.

As no standard methods were in use for the examination of lemon flavoring extracts, it was thought desirable to make an examination of the oils used. Optical methods proved most satisfactory for this purpose. The following table gives the behavior of pure oil of lemon and of the various oils and substances entering into the composition of adulterated and sophisticated lemon extracts.

	Rotation in alcohol.		Rotation of oil.	Refraction at 30° C. showing dispersion.
	Five per cent.	One per cent.		
Oil of Lemon (F. B.)	16.4	3.3	64.0	67-71
Oil of Lemon (D. B.)	16.2	3.2	63.2	68-72
Oil of Lemon (S.)	68-72
Oil of Lemon (H.)	16.5	3.3	64.3	67-71
Oil of Limes (E. & A.)	9.2	1.8	36.0	83-87
Limonene (E. & A.)	9.2	1.8	36.0	87-95
"Soluble Oil of Lemon" (F. B.)	1.7	0.3	7.0	82-98
"Citral 80 per cent." com	1.5	0.3	5.9	80-86
Oil of Lemon grass (D. B.)	-1.2	-0.2	-4.7	80-90
Oil of Lemon grass (F. D.)	-1.1	-0.2	-4.3	83-95
Oil of Lemon grass (F. B. double rect.)	-1.6	-0.3	-6.3	82-90
Oil of Citronella (D. B.)	-2.8	-0.6	-10.9	78-83
Citronella aldehyde (F. B.)	1.7	0.3	6.6	36-38
Oil of Turpentine	59-61

The rotation was determined in the Schmidt and Haensch polariscope upon the solution in a 200 mm. tube, direct and using the cane-sugar scale. The figures given in the column headed "rotation of oil" are calculated to circular degrees for comparison with standards.

The refraction is given in degrees of the Zeiss butyrefractometer, which instrument is to be had in most food laboratories. It will be noticed that many of the oils exhibit wide dispersive powers, which property proves a valuable aid in their detection in the precipitated oil obtained in small quantities from the extracts in the process to be described.

From these figures it will be seen that oil of lemon will produce a dextrorotation of about 3.4° for each per cent. of oil in alcoholic solution under the above conditions.

Soluble oil of lemon or commercial citral can only be used in amounts of 0.33 per cent. or less owing to the pronounced flavor. Upon this basis the largest quantity of these oils that could be used in an extract would produce an effect equivalent to one-tenth per cent oil of lemon (0.1° to 0.2°).

Oils of citronella, lemon-grass and citronella aldehyde are used in much smaller amounts, so that while their tendency is to counteract the optical effects of oil of lemon, their actual effect

is wholly insignificant. All are used in amounts less than one-tenth per cent.

Oil of limes is slightly more expensive than lemon oil and equally insoluble in weak alcohol. There is therefore no incentive to its use. The same may be said of limonene, but if either of these were used they would be indicated by the greater refraction of the recovered oil.

In the absence of sugar, then, the oil of lemon may readily be estimated by polarizing the extract in a 200 mm. tube and dividing the result in degrees by 3.4. A ready check may be made, and a portion of the oil may be had for examination with the refractometer, by the following process.

A flask similar to a Babcock skim-milk bottle is obtained. This bottle should have a capacity of approximately eighty cc. and have two necks. The larger tube (used for filling) should enter at the side and pass almost to the bottom of the flask. The smaller tube (used for measuring the precipitated oil) should have an internal diameter of about three mm. and a length of about fourteen cm. Such a tube will contain one cc. between its extreme graduations. This should be graduated in ten equal parts and each tenth subdivided into fifths. Each of the smallest divisions will indicate two-tenths per cent. when ten cc. of extract are used.

For the purposes of examination ten cc. of the extract are pipetted into the flask above described. About ten drops of concentrated hydrochloric acid are added (sulphuric acid must not be used) together with thirty cc. of warm water. The flask is then placed in water at a temperature of 70° C. with occasional shaking until the oil separates, which will usually take about thirty minutes. The flask is then filled with warm water by means of the side tube and may then be whirled in the centrifuge and the oil brought into the graduated neck. Fair results may be had with the ordinary Babcock bottle but the precipitation is not as complete as when more water is used and the measurement is not sufficiently exact with the small amount of extract taken.

Recovery of the oil by the above process is most complete with extracts containing five per cent. or more of oil. As a rule a six per cent. extract will yield 4.80 per cent. by precipitation, a five per cent extract 3.80 per cent., and a two and a half per

cent extract about 1.20 per cent. The results obtained by precipitation should then be corrected accordingly, after which the results should agree within two-tenths per cent. of those obtained by polarization, unless foreign optically active substances are present.

"Soluble oil of lemon" is recommended by makers to be used in amounts of about 0.33 per cent. only, but if it were used in large amount it would largely be precipitated by this method. Three per cent. may be recovered from a five per cent. solution in stronger alcohol.

The claim is frequently made that limonene, which is undesirable, is all that is excluded when an extract is made with weak alcohol and subsequently clarified with magnesia. This statement is misleading. With the limonene sample obtained from Eimer and Amend three and four-tenths per cent. was recovered from a five per cent. solution by the above method, showing that in weak alcohol (about twelve per cent.) limonene is even more soluble than pure oil of lemon.

In recovering oil from extracts containing less than two and a half per cent. oil and which are always weak in alcohol, twenty cc. of extract may be taken.

A portion of the oil precipitated may then be removed with a two cc. pipette and examined with the refractometer. If pure oil has been used the refraction will be nearly normal as given in the table.

Oil of limes, limonene or citronella oil would be indicated by a higher refraction as would also soluble oil of lemon. Citronella aldehyde and oil of lemon-grass would tend to lower the refraction but neither could be used in an extract in quantities sufficient to greatly alter it.

For the accurate determination of the alcohol, twenty-five cc. are pipetted into a 100 to 110 cc. sugar flask, and about two cc. each of a concentrated solution of aluminum chloride and disodium hydrogen phosphate are added and the flask is filled to 110 cc. with water and well mixed. The mixture is poured upon a dry filter and 100 cc. of the filtrate received for distillation. Twenty-five cc. of water are added to the 100 cc. fraction and the whole distilled to 100 cc. The alcohol is then estimated from the specific gravity of the distillate.

In most cases, however, it is sufficient to prove the absence of sugar, glycerine or solid extract by evaporating ten grams on the water-bath. These substances being absent and the specific gravity of oil of lemon (0.858) and stronger alcohol (0.820) being approximately the same, when an extract does not contain over six per cent. of oil, the alcohol may be approximated within one per cent. directly from the specific gravity of the extract.

Methyl alcohol may be looked for by adding ten cc. of a fresh one per cent. solution of sodium nitroprusside in water to an equal volume of extract and then making the mixture strongly alkaline with ammonia. A red color will appear within a few moments when wood alcohol is present. Oil of lemon does not interfere. Unfortunately this test is valueless for the detection of the more highly purified grades of methyl alcohol, such as "Columbian spirits" and "synthetic alcohol." These can only be detected by the more complicated tests as described in Allen's "Commercial Organic Analysis."

The coloring of lemon extracts is seldom from lemon peel but is generally an aniline. Curcuma is seldom used owing to its liability to fade. Indications of the coloring used are frequently yielded upon the addition of hydrochloric acid during the precipitation of the oil. Sulphonated azo dyes (tropæolins) which are frequently met with react pink or red upon the addition of the acid, and dinitrocresol is indicated by the bleaching of the solution.

The coloring-matters are best obtained by evaporating the alcohol and dyeing skeins of wool with the aqueous solution of the dye. The coloring-matter may then be identified as indicated in Allen's "Commercial Organic Analysis" and in Weyl's "Sanitary Relations of the Coal-tar Colors."

The following table gives the results of examination of a few characteristic extracts.

1. : Alcohol, 21.0 per cent. by weight; rotation 0.2° , oil of lemon less than one-tenth per cent.; coloring-matter, naphthol-yellow.

2. "Special Extract of Lemon : " Alcohol, 20.6 per cent.; rotation 4.6° , cane-sugar 1.31 per cent.; rotation due to oil 0.6° , equivalent to two-tenths per cent. oil of lemon; colored.

3. "Triple Extract of Lemon : " Alcohol, 94.3 per cent.; ro-

tation 23.1°, equal to six and seven-tenths per cent. oil ; color, lemon peel only.

4. "Ten Cent Lemon:" Alcohol, 71.7 per cent.; rotation 21.5°, equal to six and three-tenths per cent. oil ; precipitation with correction showed five and six-tenths per cent. oil ; difference due to presence of cane-sugar ; color, tropæolin.

5. "Monarch Lemon Extract:" Alcohol, 94.66 per cent.; rotation 25.7°, equal to seven and a half per cent. oil ; precipitation gave seven and three-tenths per cent. oil of lemon, having a refraction of 65°-69°.

6. "Bon-ton Extract of Lemon:" Alcohol, 22.85 per cent. ; rotation 0.1° (trace of oil) ; coloring-matter, dinitrocresol.

7. "Extract of Lemon:" Alcohol, 89.9 per cent.; rotation 20.8°, equal to six and one-tenth per cent. oil ; precipitation yielded six and two-tenths per cent. oil of lemon, of refraction 63°-68°.

8. "Double Strength Lemon Extract:" Alcohol, 54.4 per cent.; rotation 1.8°, equal to one-half per cent oil ; color, dinitrocresol.

9. "Lemon Extract from druggist:" Alcohol, 92.0 per cent. ; rotation 15.9°, equal to four and nine-tenths per cent. oil ; precipitation showed five per cent. oil, of refraction 64°-68°.

Only such extracts as fail to precipitate with water occasionally show a slight laevorotation.

ON THE DETERMINATION OF VOLATILE COMBUSTIBLE MATTER IN COKE AND ANTHRACITE COAL.

BY RICHARD K. MEADE AND JAMES C. ATTIX.

Received July 28, 1899.

SOME years ago a discussion arose between the consumer and the manufacturer of a coke as to its value. The user objected to the high ash and in support of his claim gave the analysis of his chemist, in which the ash was reported at eighteen per cent. The maker replied that the analysis was worthless as the chemist who made the analysis was probably incompetent, since he had reported nearly three per cent. of volatile combustible matter and that in a seventy-two hour coke the volatile combustible matter could not be nearly so high. The question was referred to a well-known analytical chemist. His analysis, while agreeing with that of the consumer's chemists in the percentage of ash, gave the volatile combustible matter as six-

tenths per cent. The consumer's chemists then checked their work and still found over three per cent. of volatile combustible matter. They used the method of heating a one-gram sample for three and a half minutes over a Bunsen burner and then for the same length of time over a blast-lamp, reporting the loss after deducting the percentage of moisture (found on another sample) as volatile combustible matter. A letter to the referee brought out the fact that he used a ten-gram sample and heated for the same length of time. The only excuse the consumer's chemists could give their employers was, that they used the method published in Blair's standard work on the analysis of furnace materials and products and that this was the method usually published in works on metallurgical analysis.

Of the commonly published methods for the determination of volatile combustible matter in coke and anthracite coal, none reach anywhere near even approximation. The method of Hinrichs¹ which, by the way, he recommends for soft coal and says nothing about coke or anthracite, gives far from true results; nor is the method even comparative. Heating first over a Bunsen burner and then over a blast-lamp drives off volatile matter and traces of moisture and *burns some carbon*. The loss occasioned by the latter in many cases amounts to several times that by the two former occurrences. This burning may be prevented by heating the sample in a non-oxidizing atmosphere, such as nitrogen. The loss after such a heating will represent the volatile products driven off by a high temperature. What these products are it is not our purpose to discuss. Probably even when the sample has been thoroughly dried moisture is among them.

The determination of volatile combustible matter in coke is worth doing well or worth doing not at all. If the determination of volatile combustible matter is used for checking the coking of the coal, it is an important determination of itself, and so long as the determination of the fixed carbon depends upon a knowledge of the volatile combustible matter, it is a necessary one indirectly. For, if the volatile combustible matter is one or two per cent. above what it should be, by just so much will the fixed carbon fall short of the true percentage.

The following investigation, looking toward a more satisfactory

¹Chem. News, 18, 53.

method of determining volatile combustible matter, in coke and anthracite, was undertaken by the writers over two years ago and was the outcome of the incident mentioned in the opening paragraph of this paper. The first step was to heat samples of coke in nitrogen, determine the loss and call such loss "volatile combustible matter" after subtracting the moisture, driven off by one hour's heating at 110°C . The method of procedure consisted in weighing samples of from three to four grams of coke into a small platinum dish, placing this in the crucible of the carbon apparatus described by Dr. Porter W. Shimer in the July number of this Journal¹ and passing a slow current of nitrogen through the apparatus until the air had been driven out. The nitrogen used was prepared by heating together, saturated solutions of potassium nitrite and ammonium chloride. The gas was kept in glass gas-holders, and freed from oxygen by passing through cuprous chloride dissolved in hydrochloric acid. The gas was dried just before use by passing through calcium chloride tubes, placed in front of the crucible. The exit tube from the crucible dipped into strong sulphuric acid, keeping any moisture or air from getting back into the crucible. After passing through the crucible for half an hour the current of nitrogen was slackened, a low flame placed under the crucible, the water-cooling apparatus started and the heat then carefully raised. After heating the coke for a few minutes over the full Bunsen flame, the blast-lamp was made to replace the latter and a high temperature maintained for ten or fifteen minutes. The sample was cooled in the current of nitrogen, removed, and weighed. Below are a few results upon a sample of coke which had been dried for one hour at a temperature of 110°C .

After heating three grams over a blast-lamp for fifteen minutes, the loss was found to be 0.31 per cent. After again heating, an additional loss of 0.0003 gram or 0.01 per cent. occurred.

After heating three grams for ten minutes over a blast-lamp, the loss was 0.0090 gram or 0.30 per cent. After again heating, an increase of 0.0001 gram or 0.003 per cent. occurred.

After heating three grams over a blast-lamp for six minutes, the loss was 0.0095 gram or 0.32 per cent. On again heating, the sample lost 0.0002 or 0.007 per cent.

¹ This Journal, xi, 557 (1899).

Heating in hydrogen was also tried and gave practically the same result. The losses from four determinations were 0.31, 0.31, 0.29, and 0.30 per cent.

At the time these investigations were undertaken, we supposed the idea of heating in nitrogen was original with us. A letter from Mr. W. H. Blauvelt, of the Semet Solvay Co., of Syracuse, N. Y., however, informed us that the method essentially as worked out by us was used in his laboratory and also in various technical and commercial laboratories in England and in Germany. Hydrogen, answering apparently as well as nitrogen, replaced the latter in most of these laboratories.

Samples of coke and anthracite were carefully standardized by heating in nitrogen and the volatile combustible matter then determined by various methods in common use.

The method commonly published of heating one gram for three and a half minutes over a Bunsen burner and then for the same length of time over a blast-lamp was first investigated. A sample of Pocahontas (West Virginia) coke losing, on heating in nitrogen, 0.61, 0.62, and 0.60 per cent. was used in the experiments.

We noted the following points :

Different operators get widely varying results as these determinations will show.

Operator.	Per cent of volatile combustible matter.	True per cent of volatile combustible matter.
A	3.01	0.61
B	2.51	0.61
C	2.36	0.61
D	2.25	0.61

This variation is due to the size of the crucible, the tightness of the joint between the crucible and its lid, the height at which the crucible is placed above the flame and the size of both the Bunsen burner and blast-lamp flames. A large crucible will give a higher result than a small one because the larger the crucible the more air will be present and consequently the more coke will be burned and the greater the loss will be on ignition. Below are some results on this.

Size of the crucible. cc.	Per cent. volatile combustible matter.
12	1.96
12	1.90
16	2.10
16	2.21
21	2.56
21	2.58
30	3.19
30	3.42

Since the burning takes place only on the surface of the sample, the shape of the crucible would also effect the result. In a narrow crucible the loss due to burning of the carbon would be less than in a wide one. In all of the above experiments crucibles of the usual forms were used. Of course the fit of the lid makes a great difference. Dr. Porter W. Shimer, in order to effect a close joint between the crucible and the lid, uses a thin piece of wet asbestos paper. This lessens considerably the quantity of carbon burned.

Ignition over different burners or blast-lamps gives varying results. A large flame, other things being equal, will burn more carbon than a small one. A few results will show the variation one may expect.

Burner. No.	Blast. No.	Loss on ignition, Per cent.
1	1	2.12
1	1	2.20
2	1	2.31
2	1	2.39
1	2	2.91
1	2	2.80
2	2	3.00
2	2	3.11

The results by this method are not even comparative, because some cokes burn more readily than others. A soft coke burns more readily than a hard one. A sample of Connelville coke containing 0.65 per cent. of volatile combustible matter as determined by heating in nitrogen, gave 2.31 per cent. by heating in a covered crucible. Another sample of Connelville coke gave 0.21 per cent. of volatile combustible matter on heating in nitrogen and 2.66 per cent. on heating in the same covered crucible, over the same burner and blast-lamp and under as nearly the

same conditions as it was possible to obtain. In this instance a coke containing only one third as much volatile combustible matter as another gave by this method 0.35 per cent. more.

The fineness to which the sample is reduced and the percentage of ash in the coke also probably affect the result.

As the size of the sample increases, a proportionately smaller loss is incurred by burning; there is a limit, however, to which the size of the sample may be carried, for, as the sample increases, the time required to heat the mass of coke to the proper temperature increases also, and a point is reached when the seven-minute heating fails to drive off all the volatile combustible matter. Below is a table showing the effect of the size of the sample on the result.

No. of the sample.	Loss on heating a dried sample in nitrogen.	Loss on heating dried samples of the weight indicated in a covered crucible, for seven minutes.				
		One gram.	Three grams.	Five grams.	Ten grams.	Fifteen grams.
1. Pocahontas coke	1.24	3.01	2.10	1.61	1.21	0.96
2. New River coke.....	0.32	1.69	0.93	0.69	0.55	0.47
3. Connelsville coke....	0.37	1.49	1.03	0.81	0.52	0.42
4. By-product coke.....	0.54	1.61	1.08	0.87	0.60	0.41
5. Pocahontas coke	0.28	1.52	0.90	0.69	0.40	0.38
6. Piedmont (W. Va.)...	0.31	2.87	2.00	1.31	0.96	0.54
7. Anthracite coal.....	2.85	5.10	4.19	3.01	1.87	1.03

The use of a large sample in some cases apparently reaches the same result as heating in nitrogen, but even here the result is chance. A change of burners or crucible will affect a large sample less than a small one but still quite enough to change the loss considerably. In sample No. 3, Connelsville coke, the use of a large sample in the determination shown in the table gives nearly the same result as is obtained by heating in nitrogen. But on taking a sample from the crucible and reheating in nitrogen an additional loss of 0.17 per cent. or nearly one-half of the total volatile matter was experienced, or in other words of the 0.42 per cent. of volatile combustible matter found by heating a fifteen-gram sample first for three and a half minutes over a Bunsen burner and then for the same length of time over a blast-

lamp, 0.20 per cent. was due to volatile matter expelled and 0.22 per cent. to carbon burned.

The Committee on Coal Analysis of the American Chemical Society recommend heating the sample of coal over a Bunsen burner for seven minutes. For soft coals this heating may be sufficient but for anthracite or coke the blast must be used in order to drive off all the volatile combustible matter. The committee, of course, did not recommend their method for coke analysis, or at least failed to say so, in their preliminary report.

A sample of coke containing 0.61 per cent of volatile combustible matter was heated for seven minutes over a Bunsen burner then cooled and weighed. The loss was 0.78 per cent. On heating in nitrogen an additional loss of 0.48 per cent. was experienced. The heating over a Bunsen burner in this case was only sufficient to drive off 0.13 per cent. of volatile matter.

A sample of anthracite containing 2.85 per cent. of volatile combustible matter was heated for seven minutes over a Bunsen burner and then cooled and weighed. The loss was 2.26 per cent. On heating in nitrogen an additional loss of 1.02 per cent. was experienced. The heating over a Bunsen burner in this case drove off 1.83 per cent. of volatile combustible matter.

It is regretted that the larger portion of the work involved by this investigation had been completed before the preliminary report of the Committee on Coal Analysis was published; consequently the authors were not able to apply this method upon as many samples as they would have liked.

If after heating a sample of coke or anthracite over a blast-lamp and burner for say seven minutes and weighing we again heat over the same burners and for the same length of time, the second heating will give us an approximation of the amount of carbon burned in the first. If the loss, therefore, from the second heating is deducted from that of the first the difference will agree fairly closely with the loss obtained by heating in nitrogen or hydrogen. The results, theoretically, should fall a little below the results obtained by the latter method since the volatile matter which is present in the first heating only, displaces some of the air and consequently there will be more oxygen present in the crucible during the first heating than during the second, and more carbon will be burned. To offset this, there will be

slightly less carbon in the crucible upon the second heating, and the coke will be protected somewhat by a slight film of ash formed by the burning during the first. When the sample is small this does not seem to introduce any considerable error and the results are as apt to be higher as they are to be lower than those obtained by heating in nitrogen. Care must be taken to have the conditions of the second heating similar to those of the first. The same burner and blast-lamp must be used; the position of the crucible in the flame and the size of the flames themselves must be the same for each heating.

The timing of the heats must be done with the second hand of the watch or clock and the flames must be protected from air currents and draughts. To show how closely these blanks agree and the range of accuracy of the methods some results follow.

Sample. No.	Three gram samples heated for three and one half minutes over a burner and then for three and a half minutes over a blast give per cent. loss.			
	1st. Heat.	2nd. Heat.	3rd. Heat.	4th. Heat.
1	2.01	0.86	0.84	0.88
2	0.93	0.65	0.61	0.62
3	0.94	0.51	0.56	0.50
5	0.90	0.62	0.67	0.66
6	1.03	0.67	0.66	0.72
7	3.47	0.85	0.89	0.83

By subtracting the second loss from the first we have the results in the first column below.

Sample. No.	By subtracting the second loss from the first.	By heating in nitrogen, per cent. loss.
1	1.15	1.24
2	0.28	0.32
3	0.43	0.37
5	0.28	0.28
6	0.36	0.31
7	2.62	2.85

This is the only simple method we have tried which gives results that approach anywhere near those obtained by heating in nitrogen and hydrogen. The use of asbestos paper to make a close joint between the crucible and its lid is to be recommended where this method is used. The writers have tried placing a weighed sample of coke in a crucible and covering this with a weighed amount of freshly ignited sand. While the blank

from burning does not run quite so high, it does not seem to be any more constant and the results do not seem to justify the extra weighing. It is possible that in a coke laboratory analyzing a fairly even product, a constant blank might be found and deduced, saving the extra heating and weighing.

The writers wish to acknowledge the valuable suggestions of Dr. P. W. Shimer, of Lafayette College, Easton, Pa., and to thank for their kindness Mr. W. H. Blauvelt, of the Semet Solvay Co., of Syracuse, N. Y. and Mr. G. H. Caperton, of the Fire Creek Coal and Coke Co., West Virginia.

REVIEW.

SOME RECORDS OF PROGRESS IN APPLIED CHEMISTRY.¹

The year just passed has been remarkable for the extension which the industry has undergone rather than for the development of new processes or products. Everywhere demand for products has grown and production has responded to meet it. In the United States this is particularly marked, and it is illustrated in the statistics of the imports and exports of raw materials used in the chemical arts, and of the finished product. Materials needed in the industry in this country, but not produced, or capable of production here, have been brought here in increased quantities, while the finished products have been exported in much the same ratio. We may select for illustration a few products representing the larger industries, and therefore, most widely affecting the general welfare, quoting aggregate values of the various imports.

	1897.	1898.	1899.
Alizarine products.....	\$1,022,970	\$ 886,332	\$ 700,485
Coal-tar colors and dyes	3,196,478	3,689,214	3,799,353
Glycerine	1,182,099	774,709	1,024,131
Calcium chloride.....	1,375,560	1,422,920	1,159,271
Potassium chlorate.....	458,095	308,458	173,488.
Caustic soda.....	1,147,763	476,032	252,291
Sal soda.....	82,695	40,266	20,905
Soda-ash	1,241,321	589,714	310,742

If on the other hand we consider the products exported, we find a like favorable state of affairs:

¹ Read before the New York Section, October 6, and November 10, 1899.

	1897.	1898.	1899.
Acids	\$ 102,483	\$ 115,050	\$ 207,247
Copper sulphate	415,717	1,173,186
Dyes and dye-stuffs	450,009	442,967	478,582
Calcium acetate	537,586	700,000
Medicines	2,287,744	2,460,669	2,661,008
Fertilizers	5,005,929	4,359,834	6,964,305
Glucose	2,736,674	2,871,839	3,624,890
Glue	132,581	209,441	222,072
Gunpowder and explosives ..	118,001	139,644	182,142
Glass	1,208,187	1,211,084	1,503,651
Ink, printers' and other	162,995	203,927	210,973
Leather	9,920,851	11,251,851	13,444,569
Naval stores, rosin, tar, etc..	9,214,958	9,155,144	9,982,955
Oil cake	9,611,044	12,581,534	14,531,142
Animal oils	643,924	502,332	704,127
Cottonseed oil	6,897,361	10,137,619	12,077,519
Paints	944,536	1,079,518	1,447,425
Paraffin and paraffin wax....	4,957,096	6,030,292	6,804,684
Tallow	2,782,595	3,141,653	4,367,356
Lard	20,126,485	39,710,672	42,208,462
Lard compounds	857,708	1,118,659	1,200,231
Oleo oil and oleomargarine..	7,214,917	8,290,710	9,693,362
Soap	1,136,880	1,390,603	1,457,610
Wood alcohol	140,046	199,230	414,875
Starch	1,665,926	1,371,549	2,292,973
Sugar and molasses	1,708,962	2,111,658	2,953,888
Blacking	384,937	733,658	852,187
Candles	216,565	232,214	275,470
Cement	71,160	86,208	131,161
Coal	11,008,643	11,683,749	13,661,028
Coke	547,046	608,784	632,788

The figures of the third column are for the fiscal year ending June 30, 1899, and all are taken from the late report of the Bureau of Statistics of the U. S. Treasury Department. It would seem that no stronger or more fitting illustration of the rapid advances the chemical industries are making in the United States could be needed. And it is fair to say that what is true for the United States is true for *most* of the more highly civilized countries. The depression of the past few years has been followed by a reaction, and the increased prosperity cannot fail to bring material advances in both processes and products.

During the year important expositions illustrating the advances in the chemical industries have occurred, and among the more important the Electrochemical Exposition held in Darmstadt on the occasion of the General Meeting of the Vereins Deutscher Chemiker, and the Acetylene congresses, and expositions held in Budapest and Frankfurt. In the former, the electrolytic purification of metals was represented in Elmore and Mannesmann tubes in nickel, aluminum, zinc, tin, gold, and silver; Merck's lithium, mercury, and silicon; chemicals in ammonium and sodium persulphate, pyridine and piperidine, the products of

decomposition of alkaline chlorides, carborundum, calcium carbide; and of the highest interest though not strictly belonging to the electrical products were Goldschmidt's rarer metals produced in the works at Essen. This collection included chromium copper, chromium manganese, and copper manganese, ferro-boron, ferro-titanium, and corundum showing small rubies.

In the acetylene expositions the manufacture of carbide, the apparatus for the generation and utilization of acetylene, and processes for its purification, were shown or illustrated, and the work accomplished must be of value to the advancement of the industry. In addition to the expositions a congress was held for the discussion of the questions relating to the industry.

Dr. Borchers, of Aachen, in an address before the Deutschen Elektrochemischen Gesellschaft, presented interesting statistics showing the status of the electrochemical industry in the world, and condensed the data of his detailed table in the following:

	Power existing or projected.			Value of the possible annual production.
	Water power. H. P.	Steam power. H. P.	Gas power. H. P.	
Africa—Transvaal	454	\$ 7,224,000
America—Canada	1,500	112,500
“ United States	72,300	11,750	2,500	97,506,440
Europe—Belgium	1,000	148,700
Germany	13,800	16,173	13,786,550
England	11,500	8,150	20	2,270,900
France	110,140	1,300	11,277,835
Italy	29,485	2,418,750
Norway	31,500	1,837,500
Austria	27,000	23	2,741,962
Russia	29,000	2,202,500
Switzerland ..	38,950	3,153,162
Spain	7,100	687,270

In the United States the quantities and values of the several products resulting from the industrial applications of electricity are as follow:

Product.	Quantity.	Value.
Aluminum	11,000,000 lbs.	\$ 2,625,000
Gold	154,000 oz.	4,900,000
Copper	150,000 tons.	56,250,000
Silver	49,280,000 oz.	28,350,000
Potassium chlorate	330 tons	54,037
Caustic soda	5,120 “	195,840
Chloride of lime (bleaching-powder)	11,200 “	230,000
Calcium carbide	60,000 “	4,500,000
Carborundum	560 “	140,000
Nickel	182.5 “	114,062

Borchers estimates from the results obtained in various locali-

ties that one effective horse power will yield by the various electric and electrolytic processes per annum,

16 tons	copper ;
22 "	silver ;
1.6 "	70 per cent. caustic soda, besides 3.5 tons, 38 to 40 per cent. chloride of lime ;
1.8 "	80 per cent. caustic potash, besides 3.5 tons, 30 to 40 per cent. chloride of lime ;
0.5 ton	potassium chlorate ;
1.0 "	calcium carbide ;
0.6 "	carborundum.

Of aluminum, one horse power will yield per annum, with

Volts.	Kilograms.
3	723
4	543
5	434
10	217

In 1897 we took occasion to call attention to the discussions in progress in Germany regarding the education of chemists for technical work giving expression of views concerning the requirements. The ideas there expressed have been developed in more concrete forms in the admirable presidential address of Mr. George Beilby, before the London Section of the Society of Chemical Industry in April of the present year. In his address Mr. Beilby discusses most intelligently and thoroughly, and from a practical standpoint, the educational requirements of the chemical industries, and he expresses these most clearly when he says "the scientific bases must clearly be a thorough knowledge of the principles of chemistry, physics, dynamics, and mechanics, and added to this there must be a practical acquaintance with materials of construction and the methods by which they are worked into structures. The ideal chemical engineer ought to be in thorough sympathy with the modes of thought and with the methods of working of both the chemist and engineer."

Following this idea, so comprehensive and so appropriate he offers "An Outline Synopsis of Chemical Engineering" which is in every way worthy of the most careful study and consideration of teachers of applied chemistry in our technical schools. It covers splendidly the needs of the industry not only for the present but the future ; for it will be seen that Mr. Beilby would provide first of all *chemists*, thoroughly educated in all the fundamental principles of the science. After that he would have them thoroughly familiar with the means whereby the principles of the science are to be applied in a large way. Following this admirable idea, his plan for the education of the chemical engineer would cover :

First. The scientific groundwork and fundamental principles.

Second. The materials of construction and the methods of working them.

Third. The special forms of apparatus used in the various kinds of operations.

Fourth. The general principles on which a chemical work ought to be planned and laid out.

Fifth. Works, management, and organization and manufacturing, profit, and loss.

When the plan of Mr. Beilby has been realized, we may expect that advances in the chemical industry, will receive an impulse from which most important results will flow.

In the metallurgical field, progress seems to have been in the direction of production rather than processes as has been noted in other fields of activity. The cyanide process for extraction of gold is being widely applied and it is said that forty works are being operated with it in the United States. The Peletan Clerici process dissolves the finely divided gold with cyanide solution and precipitates the gold in the same vessel by electrolysis using a mercury cathode. The yields quoted are 68.7 to 77.6 per cent. in one locality and eighty-five per cent. in another.

The mercury cyanide process of Keith uses a solution containing 0.05 per cent. of potassium cyanide and 0.025 per cent. of mercuric cyanide and precipitates the gold by electrolysis upon amalgamated plates. The Sulman-Teed process leaches out the gold with cyanide solution containing cyanogen bromide and precipitates the gold with zinc, the principal requirement being that the weight of the cyanogen bromide must be equal to one-fourth that of the cyanide. The yield in extraction by this process is claimed to be ninety per cent.

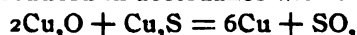
Etard proposes to extract gold with a dilute solution of muriatic acid and permanganate or the manganates of potassium or sodium and precipitates the dissolved gold with ferrous sulphate. No details of yield are given.

Smith subjects the ores to the action of nascent chlorine produced electrolytically. The ores to be treated are fed into a horizontal cylinder of wood, divided into two compartments by a porous partition, one part being lined with carbon which constitutes the anode. In the other compartment is a cathode of carbon. The ore is charged into the carbon-lined compartment with a solution of salt and the apparatus set in motion. The current is applied, chlorine is produced, and it attacks the gold present, producing aurous chloride. This substance is decomposed in the cathode compartment and the gold is deposited as a fine brown powder. Cowper-Cowles separates the solution from the ore and the gold electrolytically, using aluminum for cathodes instead of lead as recommended by Siemens. He claims that

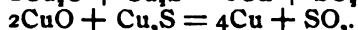
the gold adheres better, is more easily removed, and the solution is kept cleaner. The gold is not contaminated with lead and need not be cupelled.

Tomasi has further developed his process for desilverization of lead by electrolysis. A rectangular cell enclosing fixed anodes is used and between these anodes of crude argentiferous lead is found the cathode consisting of a disk of aluminum bronze which may rotate at the rate of one to two turns per minute. Only a portion of the disk is immersed in the electrolyte which consists of lead and potassium acetate. The finely divided lead is removed from the cathodes by brushes and collected. The silver falls as anode mud. The physical condition of the lead obtained is most favorable for oxidation.

In the extraction of copper the Herreshoff progressive and continuous roasting furnace has attracted the most favorable attention. It consists of a vertical cylinder divided into sections by horizontal diaphragms, the alternate diaphragms having openings at the center and periphery, respectively, the ore being moved forward and downward by properly arranged rakes the arms of which are attached to a vertical shaft passing through the middle of the cylinder. James and Nicholls, of Swansea, carefully roast the properly concentrated ore and transfer it to a second roasting furnace where it is mixed with a given quantity of fresh unroasted concentrate whereby the copper oxide of the first operation is reduced in accordance with the following :



or



They claim saving of time, labor, furnaces, loss of noble metals: a high yield of copper, very pure sulphurous gas. Keller considers the purity of the copper obtained not greater than that from the reverberatory furnace process and below that of the Bessemer process.

The Hoepfner process for extraction of copper seems to be extending notwithstanding the unfavorable criticism. It is stated that new works at Papenburg will extract daily about 1000 kilograms of copper. The ore is finely pulverized in a Krupp mill, leached with copper chloride solution, the copper, lead, nickel, and silver extracted, while the cupric salt is reduced to the cuprous condition. The solution is purified, freed from silver, and caused to flow through compartments having carbon anodes and copper cathodes. The chlorine separating at the anode is taken up by the copper solution and the regenerated cupric liquor is heated and returned to a new lot of ore. From Rio Tinto ores with 3.37 per cent. of copper, ninety-one per cent. of the metal was recovered after four hours' treatment and only three per cent. of the iron content dissolved, while by a longer extraction

period 98.5 per cent. of the copper is secured and only four per cent. of the iron taken up. It is claimed for this chloride process that with eight-tenths of a volt ninety per cent. of the current is utilized so that one horse power in twenty-four hours will produce fifty-four kilograms of copper against fifteen kilograms by the sulphate process. Hoepfner claims that by this process the electrolytic recovery of lead, nickel, silver, and zinc has been solved, and discusses the modifications in the process involved.

In the extraction of nickel the process of Mond has been further developed by the construction of extensive works at Southwick in England. The product from the Bessemer process is used. It is first roasted and then contains thirty-five per cent. of nickel and forty-two per cent. of copper, and about two per cent. of iron. The nickel content is then increased to fifty-one per cent. by extraction of part of the copper with vitriol, the residue then transferred to the vertical plate furnace, and the copper and nickel reduced with water-gas hydrogen at a temperature not above 300° C. without reducing the iron. The nickel is now volatilized below 100° C. as the carbonyl compound in the plate tower. After a time the residue is returned to the reducing tower, and thus wanders back and forth between both ovens seven to fifteen days when sixty per cent. of the nickel will have been removed. The carbonyl compound is decomposed at 180° C. and the nickel deposited on iron plates or in a granular condition, while the carbon monoxide is returned to the furnace. The metal obtained contains 99.8 per cent. nickel and it is claimed that the process may compete with others for the extraction of the metal.

Storer's method seems to have the attraction of being inexpensive and simple. He treats ores containing silicate, hydrate, or oxide of nickel with ferrous chloride solution,—one part of ore with 2.75 parts of solution containing 26.5 parts of the iron salt,—in a closed vessel heated to 187° C. with live steam and with corresponding pressure. After five to eight hours' digestion, and double decomposition has been effected, the vessel is emptied, the iron oxide produced is collected, and washed to be used as pigment, while the nickel may be separated from the solution by electrolysis or by precipitation. About 750 pounds of ferrous chloride are consumed per ton of ore.

The metallurgy of zinc has been practically stationary. Jones subjects the ore to oxidizing and roasting, leaches the ore with water or weak acid, separates the iron with ammonia, filters and electrolyzes in a cell with a diaphragm, adding ammonium sulphate to the anode space. Kohler heats the roasted and oxidized ore with ammonium sulphate, leaches the residue, and precipitates the solution to recover the zinc as hydrate. Bechi mixes the ore with "Abraumsalz" or common salt and roasts the mixture.

Then he leaches the residue, heats the solution with zinc hydrate, whereby copper is precipitated and zinc chloride left behind. This latter may be decomposed by lime, or the zinc may be separated by electrolysis. Schultz finds that zinc chloride ordinarily electrolyzes with difficulty and that presence of water is unfavorable. He evaporates the solution almost to dryness and mixes with strong hydrochloric acid, when, it is declared, electrolysis becomes easy and the deposit fine.

The process of Goldschmidt for obtaining high temperatures and the reduction of refractory metallic oxides by combustion of aluminum has been further developed. The aluminum used must be finely divided and intimately mixed with the oxide to be reduced. The mixture is ignited by adding a strongly oxidizing agent such as barium dioxide and after being started may be made continuous. The alumina slag solidifies as corundum and may be used as abrasive material or for the manufacture of aluminum. The method is employed for production of alloys and for welding. For the latter purpose an impure aluminum serves perfectly well. Kupfelwieser has made a careful study of the method of Goldschmidt. He finds the heat of combustion of aluminum to be 7140 calories and gives the following data representing the requirements for production of one kilogram of:

	Iron.	Manga- nese.		Sili- con.	Chro- mium.	Tung- sten.
Compound used.....	Fe ₂ O ₃	MnO ₂	Mn ₂ O ₃	SiO ₂	Cr ₂ O ₃	WO ₃
Aluminum required.....	0.484	0.656	0.492	1.272	0.520	0.294
Heat developed, calories.	3456	4684	3512	9082	3712	2099
Heat consumed:						
(a) for reduction.....	1796	2115	2000	7830	2200	1100
(b) for melting slag....	548	742	550	1439	582	324
(c) for melting metals...	362	535	535	435	434	360
Total heat used.....	2706	3392	3091	9704	3216	1784
Excess to cover losses, etc.	750	1292	421	672	497	315

Silicon has been produced in the electric furnace. Hyde has thus produced the crystalline and graphitoid form, and so likewise has De Chalmot. The latter obtains a mixture of copper, silicon, and copper silicide. The copper is separated with nitric acid and the liberated silicon freed from silica with hydrofluoric acid. The Fabrik Elektrometallurgischer Produkte zu Frankfurt-Bockenheim, have, by a secret process, brought into the market rods of silicon which they specially recommend for use in manufacture of iron and steel. In iron it increases the graphite, reduces the shrinkage of castings and the tendency of liquid iron to absorb gases. For low carbon steel it is desirable because it effects the necessary reductions without introducing carbon. The same firm offer copper silicide in eight to nine kilogram bars, containing ten, fifteen, and thirty to thirty five per cent. of

silicon. This compound serves for deoxidation of copper instead of copper phosphide. Silicon increases the strength but reduces the conductivity of copper containing it. These relations are as follows:

	Strength per square millimeter. Kilograms.	Con- ductivity.
Pure copper.....	28-35	100
Copper with 0.5 per cent. silicon	50	28
Copper with 3.5 per cent. silicon.....	95	7

But the compound is useful in the form of bearing metal, strong wire, and sheet, for resisting acid gases and vapors.

The production of phosphorus in the electric furnace has been extended, and this is not the only application of the current to high temperature distillations. Several forms of furnace have been devised for heating materials with exclusion of air and with reducing media, together with condensation and collection of the volatilized products. Many attempts, more or less successful, have been made both in this country and abroad to apply them to the production of phosphorus. In most cases the calcium phosphate is heated with excess of carbon, liberating the phosphorus and leaving calcium carbide behind. In other cases, as in the furnaces of Albright and Wilson, the phosphate is mixed with sand as well as carbon. Harding makes a tolerably pure phosphoric acid, and this, mixed with carbon, is charged to an electric furnace with an outlet at one side for slag. A hollow electrode projecting through the bottom is connected with a carefully controlled supply of volatile hydrocarbon, such as gasoline, and the phosphorus liberated and volatilized is carried off through a pipe at the top of the furnace. Hasenclever discussing the progress in sulphuric acid manufacture in 1898 calls attention to the improvements made by the Badische Anilin und Soda Fabrik in the application of the contact reaction of Winkler, whereby combination of sulphur dioxide and oxygen is effected by passing the gases over platinized asbestos or pumice. They found that the heat generated by the reaction tends to so heat the after-end of the contact mass as to cause it to induce a reverse reaction and the reduction of the sulphur trioxide to the dioxide. To prevent this they cool the contact mass either by currents of air or gases about it, or by baths of fused metal, and the cooling is so carefully controlled that the reaction is practically quantitative. Besides the very much larger yield obtained, injury to the apparatus, and weakening of the contact mass are diminished.

Another important requirement of the successful application of this reaction is that the gases shall be free from dust and injurious impurities such as arsenic, phosphorus, mercury, etc. If washed with water, the gas must subsequently be dried, and it must be chemically and optically free from dust.

Meyer proposes the use of cylindrical instead of rectangular chambers in the manufacture of sulphuric acid, and recommends spiral circulation of the gases. In the application of the idea the gases from the Glover tower are made to enter tangentially at the periphery of a vertical cylindrical chamber and at about mid-way between the top and bottom. Circulating about they pass out at the center of the bottom and pass along to other chambers which may be similarly cylindrical or of the rectangular form. The outlet, to provide against destruction of lead connections which had been found to occur, is of stoneware of special construction, and to increase the cooling surface a cylinder is let into the center of the top of the chamber, and circulation of air induced by an open pipe hanging within the cylinder. The air flows down through the annular space thus made and up through the pipe. Numerous economies are claimed for the system.

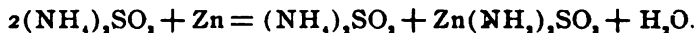
Hydrogen sulphide is formed in considerable quantity as a by-product in asphalt refining in the works of the California Asphaltum Works at Ventura, California. It is burned to sulphur dioxide, and this in turn is converted in chambers in the usual way to vitriol yielding daily ten tons of finished acid of very high purity.

Mourlot produces magnesium sulphide in the electric furnace by heating together, in molecular proportions, magnesium chloride and tin sulphide, with a current of 50 volts and 2000 amperes. Tin chloride is formed and volatilized while magnesium sulphide remains, partly or wholly fused. The latter product is not attacked by the carbon of the anode, is less sensitive to the action of water than the powdery form which decomposes suddenly under such influence, but in the presence of steam, it breaks up quickly with formation of magnesium oxide and hydrogen sulphide.

It is well known that when an acid sodium sulphite is treated with zinc, three molecules enter the reaction and sodium hydrosulphite and double sulphite of sodium and zinc are formed.

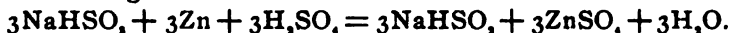


But Prudhomme finds that if ammonium bisulphite solution be neutralized with ammonia, and the whole poured over zinc, the reaction, as written by him, becomes :



The zinc salt is insoluble and may be separated by filtration. The advantages of this reaction are : direct formation of a neutral salt less easily oxidized than the acid salt with ninety-six to ninety-eight per cent. of the theoretical yield ; utilization of half the bisulphite treated ; production of neutral hydrosulphite free from zinc salt by simple filtration.

Grossmann's process is still more economical as regards consumption of bisulphite. Taking a solution of the salt of 60° Tw. and containing twenty per cent. of total sulphur dioxide, he mixes it with sulphuric acid and zinc dust in accordance with the following reaction:



He found that the liquor so produced has three times as much reducing power as the ordinary zinc bisulphite bath in indigo-dyeing and considers it a distinct improvement upon the bath heretofore used.

The electrolytic production of chlorine and its compounds has undergone considerable increase during the past year. Hasenclever says the extension of electrolytic chlorate manufacture both in Sweden and French Switzerland has been so active that the price has fallen in Germany from 100 to 120 marks per 100 kilograms to about 55 marks, and that many manufacturers have resorted to manufacture of other products particularly carbide.

Production of chloride of lime has grown to such an extent that increasing quantities are available for export. John Brock, president of the United Alkali Company, stated to the stockholders that while in 1895 the export of soda from England to America was 125,698 tons, it had fallen to 29,393 tons in 1898. During the same period caustic fell from 33,625 to 11,171 tons, and chloride of lime suffered in the same way. The company had established works at Bay City, Michigan, to supply the American market under the title, The North American Chemical Company.

The National Electrolytic Company, of Niagara Falls, now use 1100 horse power supplied by the Niagara Falls Hydraulic Power Company in the production of potassium chlorate, using the process of W. T. Gibbs applied to potassium chloride from Stassfurt. They are now doubling their works.

The cell and diaphragm of Hargreaves and Bird have at last been authentically described. The cell is made up of two parts, the anode compartment and the cathode space. The former consists of a leaden box, pitched inside and further lined with a wall of Portland cement. Bolted to each side of this is a cast-iron box which encloses the cathode space. If the cell be horizontal, only one cathode space is provided and constitutes the bottom. The anodes consist of rectangular carbon slabs which are arranged parallel with each other, the edge of one overlapping that of the other, forming a sort of horizontal grating in the horizontal cell and sustaining walls in the vertical ones. The anodes project through the one wall and rest in depressions in the other, the outer ends being covered with lead or type metal connected with each other by metallic conductors. Between the

anode and cathode spaces is the cathode diaphragm peculiar to the Hargreaves cell. It consists of iron gauze upon which has first been floated paper or asbestos pulp. This is covered with Portland cement in moist thin layer, and for protection this in turn is covered with porous fibrous material such as asbestos cloth, wool, or other similar substances. For easier removal of the product the layer next the gauze is impregnated with some soluble substance which, in the first operations, washes out, leaving narrow spaces about the wires of the cathode.

When the cell is set up the anode space is filled with the electrolyte solution, and solid electrolyte (salt) is fed in through an opening in the top which is closed, when the cell is in operation, by a stoneware lid resting in a water seal. In the horizontal cell the solid electrolyte rests upon the anodes and in the vertical cell is held between the two rows of anodes. Inlets and outlets are provided for the circulating electrolyte solution, and for exit of chlorine. If the solid electrolyte contains too much insoluble impurity it is dissolved in a separate vessel through which the liquid electrolyte is made to circulate. Steam is fed to the cathode space and the caustic dissolved flows out through the bottom.

One of the criticisms of the Hargreaves cell has been that the alkali produced is contaminated with salt. This difficulty has been overcome by the application of the fact observed by Hargreaves that when salt solution containing but little sodium carbonate is evaporated, the carbonate content increases and the mother-liquor contains salt and carbonate in the molecular ratio of 2 : 1 ; and furthermore that on boiling salt crystals or a crystal mixture of salt and carbonate (the monohydrate) with a large quantity of concentrated soda solution, the salt will be dissolved and separated from the monohydrate. Hargreaves has devised a system of pans and crystallizing vessels for effecting such separation.

The method of circulation of the cathode mercury of the Castner-Kellner cell has been the subject of modification at the hands of several inventors with more or less advantage. G. and G. W. Bell having in view both this and the saving of cell space, erect three columns of shallow trays, the trays of the middle column being much larger than those of the other two columns. Communication is established between the trays of the middle column and those of the same level of the outer columns respectively in such a way that when the cells are charged with mercury a perfect seal between them is established. Inlets and outlets for circulation of electrolyte in the outer series of cells is provided, and each anode cell has likewise an outlet for chlorine communicating with a general conduit. The cells are firmly held together by bolts passing vertically through all. The anodes

project horizontally through the anode cell walls, each tray being provided with the necessary anodes. Water is fed to the trays of the middle column and may be caused to circulate. With the apparatus properly set up, charged with mercury and electrolyte and the current operating, the chlorine outlet of one series of anode cells is partly closed and pressure thus generated within the cells drives the mercury toward the other columns. After a proper time this outlet is opened, the pressure released, the outlet of the other column partly closed, and the current of mercury reversed. The mercury is thus made to oscillate back and forth between the anode cell and the so-called cathode cell, but really the decomposition cell, and the reaction completed.

The Electron Chemical Works effect a circulation of the mercury by means of a steam injector, whereby the mercury is atomized or pulverized in contact with steam. The latter is decomposed by the alkali metal, an excess being condensed to dissolve the hydroxide produced. The mercury is led back to the electrolytic cell by gravity and the circulation thus maintained.

To obviate the difficulty arising from the diffusion of the anode and cathode products in apparatus having a mercury cathode, the Solvay Company resort to superposed strata of electrolyte of different densities and maintain these densities by careful circulation of the liquid of the strata through boxes containing the solid electrolyte. Vertical diaphragms across the ends of the cells and extending to different depths serve to establish the layers and the circulation of the strata of liquid is maintained by pumps.

Acker decomposes fused salt over melted lead, producing chlorine and sodium lead alloy. The furnace consists of two concentric cylinders of magnesite. The inner cylinder really constitutes a bell hanging within the outer cylinder. The bottom of the furnace is of iron, and the cathode passes through it. Fused lead is fed through the bottom until the mouth of the bell is sealed and the current is applied while the anodes within the anode space is in contact with the lead. These are withdrawn until an arc is produced, and salt is instantly charged to the annular space. Chlorine is generated and is led away through an outlet provided for it, and the sodium liberated combines with the lead. The alloy, which is lighter than the metal rises within the bell and overflows through a tube passing out at the bottom. No data regarding the operation and efficiency of the furnace are given.

Muspratt and Smith find that the requirements of successful operation in manufacture of high strength hypochlorite solution, are: Continued excess of alkali in solution, low temperature, below 80° F., a gravity of solution at which salt deposits most readily, prompt and complete removal of scum if present, and periodical introduction of caustic. The stability of the product

depends upon the absence of iron and the maintenance of such strength that salt does not deposit. The authors declare that under favorable conditions, solutions containing thirty-five per cent. by volume of available chlorine may be made, and such a solution is, excepting unmerchantable strengths of hydrogen peroxide, the strongest oxidizing agent known.

It has been found that electrolytic chlorine does not give a good yield of chloride of lime, and Sindig-Larsen ascribes this to the fact that electrolytic chlorine is more active than that produced by chemical methods and believes that the oxygen is replaced producing calcium chloride. To avoid this he carefully dries the gas by passing it over calcium chloride, and then heats it by passing it through tubes heated to 700° or 800° C. Then it is cooled and passed into the lime chambers in the usual way.

Dr. Erich Muller finds that the efficiency of electrolysis in the production of oxidized salts of chlorine, bromine, or iodine, is greatly enhanced by the addition of a small proportion of potassium dichromate. Thus with a thirty per cent. salt solution he obtained 32.8 per cent. current efficiency, while with a similar solution under practically like conditions, but containing 0.18 per cent. of potassium dichromate, he secured 69.6 per cent. of current efficiency. The current efficiency in the production of iodate was ninety-seven per cent. while 97.6 per cent. of bromide was converted to bromate corresponding with ninety-four per cent. efficiency.

Meister, Lucius, and Bruning oxidize chromous salts by electrolysis in presence of sulphuric acid with a current of three and five-tenths volts, and 300 amperes and a temperature of 50° C. The operation is carried out in a leaden vessel with a diaphragm. When the anode liquid is fully oxidized it is removed and the cathode liquid transferred to the anode cell and the cathode cell filled with fresh solution. To obtain the best results a solution of high conductivity is recommended and the proportion of 100 grams of chromic oxide, and 350 grams of sulphuric acid seem to meet this condition.

The Neustassfurt Salt Works oxidize manganate to permanganate by electrolysis in a vessel in which the cathode cells filled with water are suspended in the anode liquid in which the manganate is dissolved. Upon application of the current the manganate is oxidized and potassium hydroxide is liberated in the cathode cell. When the strength of the hydroxide reaches forty per cent. the permanganate is nearly insoluble, and precipitates. To maintain the proportion of manganate this salt is suspended in the anode liquid in vessels with perforated bottoms. The process may be made continuous.

To prepare oxygen, Stewart fuses a mixture of sodium

manganate and hydroxide, the proportions of the constituents being such that fusion occurs at 375° to 400° C. The fusion is effected in cast-iron vessels and air is passed through the mass. When, after a few minutes, absorption of oxygen is complete, air is cut off and steam admitted. Oxygen is promptly evolved and decomposition is soon complete. The operation is then reversed. Four retorts, two feet square and eight feet long, are said to have a capacity of 140 to 150 cubic feet of oxygen daily. Hitchcock declares that when oxygen is used with bleaching-powder the efficiency of the latter is increased, and a saving of thirty to forty per cent. is effected.

Ladenburg condenses ozone by cooling it with liquid air and fractional distillation of the ozonized oxygen. Oxygen passes off until the volume is reduced to ten per cent. when evaporation ceases. The product thus obtained has a dark blue color, contains 86.14 per cent. of ozone and has a density of 1.3698 compared with oxygen. From this the density of ozone was found to be 1.456. The liquid ozone boils at -125° C. but at once explodes violently.

The commercial production and utilization of ozone is extending. Kershaw discusses the more recently improved forms of apparatus for the purpose and particularly those of Andreoli, Otto, Yarnold, and Siemens and Halske, describes their construction and operation and presents data of yield obtained and cost of energy employed to produce one kilogram of ozone and active oxygen respectively as follow :

Form of ozonizer.	Yield of ozone per H. H. P. hour Grams.	Cost of electrical energy per kilo of ozone.	per kilo of active oxygen.
Yarnold	175	\$0.57	\$0.513
Otto	150	0.20	0.60
Andreoli	94	0.30	0.954
Siemens and Halske	20	1.50	4.50

According to Kershaw ozone produced by the apparatus of Yarnold, Otto, and Andreoli is three to four times as expensive as bleaching-powder and about fifty per cent. more expensive than sodium bichromate, as a source of active oxygen. Engledue places the cost of ozone produced by the Yarnold apparatus at about five and one-fourth cents per pound, of active oxygen at about fifteen, and of one electrical horse power at two cents. The successful production of ozone requires absence of heating in the apparatus and that the air to be ozonized shall be thoroughly dry and free from dust. Engledue proposes many uses of ozone including bleaching of oils and in this latter is supported by Ronco who declares that in the practical operation, the cost of handling, daily, five tons of oil effectively, was 45 francs. Andreoli recommends purification of water with ozone and states

that after treating water containing from 6,000 to as high as 110,000 microorganisms per cubic centimeter, in eleven trials, no active organisms remained; in ten other trials ten organisms per cubic centimeter were found, and the largest number found after four other trials was forty.

The production of liquid air is progressing and it is fair to believe that it will find practical applications. A company has been established in New York City for the manufacture of liquid air and claim a daily capacity of 1,500 gallons. Facts regarding cost of the product are not easily obtainable but there is reason to believe that it can be produced at low expense.

Hempel declares that with Linde's machine, one horse power hour will yield one cubic meter of air containing fifty per cent. of oxygen. He states that though its chemical uses thus far have been confined to making an explosive by mixing with carbon, and to producing chlorine in the Deacon process, it should also serve a useful purpose in making producer gas whereby, in the product, the carbon monoxide, marsh-gas, and hydrogen would be increased about 100 per cent. and the nitrogen reduced to a corresponding extent. It should also be used for increasing the efficiency of combustion of ordinary fuels, in the operation of gas engines, in connection with the Bessemer process and in the manufacture of sulphuric anhydride by the contact process. He would furthermore use the nitrogen in a concentrated state for the production of nitrides and cyanides.

In the past couple of years the production of white lead has received marked attention and many new and promising processes of manufacture have resulted. Beilly, Cox, and Hey volatilize the metal in an electric furnace, subject the vapor to the action of air and steam, carbon dioxide, and acetic acid. The resulting reaction occurring is said to yield white lead of high quality. Cook and Clark on the other hand subject finely divided lead to the action of water and air and claim production of the hydroxide. This is separated by levigation from the unoxidized metal and the process continued until the metal is all oxidized. The hydrate is used as such or is carbonated with gas to produce white lead. In the Mathews process the ground oxidized product is digested a short time with a solution of lead oxide in glycerine and acetic acid and the solution filtered. The filtered liquid is then treated with pure carbon dioxide to proper saturation, the fine white precipitate of basic lead carbonate separated and washed in a filter press. The mother-liquor and washings are returned to the beginning of the operation. The cake from the filter-press is carefully dried and is in such condition that mill-grinding is not needed. The solution contains seven to seven and a half per cent. of glycerine and this seems essential to the proper precipitation of the

product. It is claimed for the process that white lead can be produced by it at greatly reduced cost and that its color and general physical properties are superior to those of the product obtained by the corrosion process.

Galloway's process depends upon the decomposition of lead nitrate with ammonium carbonate under pressure.

The Elektrochemische Industrie Gesellschaft (Köln) have improved upon the process of Luckow. In the new process the anion of one salt serves to dissolve the anode and the anion of the other salt precipitates the dissolved metal. The first salt is present in the proportion corresponding with the highest conductivity of its solution, while the second which serves to precipitate the metal in the insoluble condition is calculated from the electrochemical equivalent related to the current strength. It is by this rule found that seven per cent. of sodium chlorate and 0.011 per cent. of sodium carbonate are the proportions of these substances in solution best suited to the electrolytic production of white lead using hard lead anodes and soft lead cathodes; ten anodes and eleven cathodes, each with a surface of twenty by thirty cm., are suspended in the solution, fifteen cm. apart. During the electrolysis, with a current of five-tenths ampere per square decimeter and one and two-tenths to one and three-tenths volt at a temperature of 15° to 17° C., carbon dioxide is carefully injected into the solution through fine jets for the regeneration of the precipitation salt and circulation of the liquid.

Bradley and Jacobs have developed an interesting reaction in the electric furnace. They find that if barium sulphate be heated with a limited supply of carbon, part of the sulphate is reduced to sulphide and the sulphide reacting upon the residual sulphate converts it into oxide with the production of sulphur dioxide. The oxidation of the sulphide is not complete and the product in actual practice contains about forty per cent. of sulphide.

To avoid glazing the surface of barium carbonate when heating it to prepare barium dioxide, Feld encases the furnace with iron and uses fuel producing no vapor of water in burning, thus excluding all moisture from the furnace. Knoop renders phosphorite and other similar phosphatic material citrate-soluble by heating it with silica and alkali salts, and after an extended experience finds a mixture of chalk sand and alkali sulphate with the phosphate to give the best results and to make ninety-nine per cent. of the phosphate soluble.

Mabery and Baltzley recommend the use of sodium aluminate for removal of lime and magnesia from water and claim to have removed from water ninety-eight per cent. of these substances

even when the quantity of reagent used was less than was required by theory. Their paper on the subject is to be found in the pages of this Journal.

The extension of manufacture of coke with recovery of gas and by-products is increasing both in Europe and this country. In the latter they have been established at Halifax, Nova Scotia, Boston, Mass., Glassport, Penna., Benwood, West Virginia, and Ensley, Alabama. The operation of these furnaces has been discussed by Pennock in our own Journal and by Hoffmann in the *Engineering and Mining Journal*. The latter authority states that in Halifax, where the Semet-Solvay ovens are built in groups of ten, each retort is charged with five tons of coal which is coked in twenty hours. The gas-pressure is 1.25 cm. and the temperature of the oven 1000° to 1100° C. The coal used contains about sixty per cent. of fixed carbon and the gas produced having over sixteen candle power is used for lighting and the remainder for heating. Thirty-seven tons of coal coked in twenty-four hours yields 31,000 cubic feet of gas, of which 32.26 per cent. is illuminating gas and 67.74 is power-gas. The coal contains nine and nine-tenths per cent. of water of which four per cent. is hygroscopic. The results obtained at Glassport, using Youghiogeny coal, are of interest.

Products from one long ton of coal.		Pounds.	Per cent.	
Coke {	Large coke > one inch.....	66.69	1593.4	71.13
	Small coke a half to one inch..	1.64		
	Breeze < one inch.....	2.80		
Tar.....		75.7		3.38
Ammonia (= 1.373 sulphate).....		7.6		0.34
Gas, total 10,390 cu. ft. of 0.466 sp. gr.		368.0		16.43
Sulphur compounds in gas.				
Hydrogen sulphide, 0.98 lb. per 1000 cu. ft.		10.8		0.48
Carbon disulphide, 0.13 " " " "		1.6		0.07
Gas liquor and loss by difference		182.9		8.17
		<hr/>		<hr/>
		2240.0		100.00

49.5 per cent. of the gas was surplus, not needed for heating the ovens. The coke contains 8.91 per cent. of ash, 1.27 per cent. volatile matter, 0.0041 per cent. phosphorus, and 3.67 per cent. water. The tar recovered is preferable to gas-tar for distillation.

Muller shows that benzene is appreciably soluble in water and that this should be taken into account when large volumes of water are used in the scrubber for purification of the gas. Absorption varied with the proportion of benzene and from about three to eight per cent. of that present. Paraffin oil absorbs practically all the benzene and is used in the determination of that present in coke-oven gas.

According to Scheithauer, if 100 cubic meters of gas from oil be compressed to twelve atmospheres, six to eight kilograms of liquid hydrocarbons are separated and the gas loses twenty-five per cent. of its illuminating power. The condensed liquid contains seventy per cent. of benzene, fifteen per cent. of toluene, five per cent. of higher homologues, and ten per cent. of ethylene homologues.

The production and utilization of calcium carbide have made some advances and many of the difficulties involved have been obviated. The subject has been discussed so clearly and with such manifestly high authority by Wolff in an address before the Berlin Section of the Vereins Deutscher Chemiker that it seems important to present here a somewhat detailed abstract of what he has set forth.

He gives Moissan the credit of being the original producer of carbide in a large way declaring that Bullier and Willson followed and made their discoveries practically simultaneously, but with no knowledge of each other's work. The industry had extended so that in the autumn of 1897 the power consumed thereby in Germany was 6,000 to 8,000 horse power, in Norway 19,000, while works are projected in the Tyrol and other localities in Austria, in Switzerland, France, and Sweden. He states that in 1897 the production amounted to 10,000 tons. Yet in spite of the wide extension of the production he expects little reduction in the price of the product. The cost depends upon three factors: 1, cost of power; 2, price of raw materials; and 3, yield. All these naturally vary greatly. Mode of operation, plans of furnaces, construction, etc., likewise influence the results. Saving of heat is one of the most important and the author commends Pictet's plan of previously heating the charge by means of gas and the oxyhydrogen flame, thus saving the current. He finds the cost of carbide at the works at Vernier, near Geneva, to be 157 francs, say, \$31.40 per ton (1000 kilograms).

Discussing the danger from explosion of acetylene, he ascribes it to two causes: 1, carelessness; 2, the chemical and physical properties of acetylene. The first cause is avoidable by bearing in mind that ordinary gas and air mixtures have explosive limits of between eight and twenty-eight per cent. while acetylene air mixtures which contain three to eighty-two per cent. of acetylene are explosive. Under ordinary pressure acetylene is not explosive. Under high pressures and liquefied it may be. His conclusion is that acetylene is no more explosive than any other burning gas; but it may be and is dangerous under false conditions and in bad apparatus.

His experience with producers leads him to recommend unqualifiedly the apparatus of Pictet in which the carbide is

allowed to fall into a large volume of water and for purification he recommends the method of Frank, subjecting the gas to the cleansing action of acid metallic salts. Yet because of the many inconveniences due to ammonia and sulphides in the gas he prefers his own; that is, washing the gas in calcium chloride solution to remove ammonia and sulphides, and then passing it over chloride of lime to oxidize the phosphorus and other compounds.

For burners he particularly recommends two of special construction based upon the Bunsen principle. The first consists of two tubes pointing toward each other at right angles, the jet from one impinging upon that from the other. The gas issues from a small aperture in a tube surrounded by four air-holes, so that the gas issues from the tip mixed with air. The other consists of a small metal tube with a slit burner of lava like ordinary gas-burners. The gas issues from a small aperture surrounded by air-holes and mixed with air issues from the slit burner. These forms prevent overheating and consequent decomposition of the gas before burning and avoids deposition of heavy decomposition products in the slit. The cost of the gas to consumers must naturally vary. Compared with illuminating gas at say \$1.20 per thousand cubic feet and acetylene at \$10.50 for the same quantity, the ratios for sixteen candle power of light become:

Acetylene.....	\$1.65
Gas, slit burner.....	3.00
Gas, Welsbach.....	0.54
Electric incandescent lamp.....	3.50

With gas at sixty-five cents per thousand, the price paid in New York at the present time, the figures for light with that substance would become 1.50 and 0.27. Under any circumstances therefore acetylene could not compete with gas in Welsbach burners but it would be less expensive than electric light.

Lewes recommends the use of acetylene in admixture with water-gas and Julius Pintsch mixes thirty-five volumes of acetylene and sixty-five volumes of oil-gas for use as illuminating material. This mixture may be compressed to six atmospheres without danger of explosion.

Pictet's method of purification of acetylene consists in passing the gas through a calcium chloride solution cooled to -20° C. and then through concentrated sulphuric acid cooled to -40° C. It gives excellent results. A. Frank uses a mixture of one part copper chloride and eight parts hydrochloric acid. Acid-resisting vessels are naturally necessary. Wolff recommends chloride of lime (bleaching-powder) mixed with chromic acid salts. Ullman recommends chromic acid alone and finds that it removes both phosphorus and sulphur. He considers it the most effective purifying agent thus far used.

Berthelot and Vielle find that when acetylene is mixed with other gases, such as hydrogen and illuminating gas, the pressure limit for explosibility approaches that for acetylene alone, and particularly as the content of acetylene grows. The law is independent of the inert gas. Emerson Reynolds made experiments on the influence of carbon dioxide on the illuminating power of acetylene. Five to eight per cent. of carbon dioxide reduces the smokiness of the flame and especially prevents clogging the burners. Increase in illuminating power was not marked, but the mixture containing five per cent. of carbon dioxide gave as much light as acetylene alone and there was, therefore, reduction of the volume of acetylene burned. Carbon dioxide probably has some oxidizing effect.

To undertake a discussion of the forms of furnace for manufacture of carbide would be impossible within the limits of this paper. The principal improvements depend upon continuity of operation, saving of heat generated in the operation by applying it to increasing the temperature of the charge or heating the charge from external sources in order to reduce the consumption of heat of the arc.

Bradley and Horry obtain more or less of continuity of operation by causing the charge to meet the electrodes in the periphery of a wheel or cylinder, so that the carbide formed in blocks at one side may be removed more or less cooled at the other side. The production of dust seems to be one of the prime difficulties occurring in the operation of this furnace.

Kenevel, Spofford, and Mead use horizontal revolving cylinders as electrodes in the bottom of a vertical shaft and so aim at continuity. Roberts feeds the charge from a hopper upon the electrodes, arranged horizontally above a movable apron or endless belt. The electrodes are brought into contact covered by the charge, the belt set in motion, the electrodes gradually separated, and the motion of the belt graduated to the speed of formation of carbide between the electrodes. The carbide lies in a bed of material of the charge and is covered with it. It, therefore, has an opportunity to cool with partial exclusion of air. Pictet heats the charge in a vertical shaft on its way down to the electrodes, nearly to the temperature of the reaction, thus saving electrical energy. His furnace is being used by the Ingleton Carbide Company in England. Memmo charges a mixture of calcium hydroxide and carbon and uses the water-gas said to be formed in the furnace for heating the charge. But these problems presented in the carbide manufacture are not easy and they still await perfect solution.

Hintz and Bunte, independently of each other, have made experiments with Welsbach mantles to determine the best mixture to use in their manufacture, to secure the highest efficiency

find that the mixture of pure thorium oxide with pure cerium oxide is best, and that the presence of other oxides such as neodymium, zirconium, lanthanum, and yttrium are rather detrimental than otherwise. They find that the efficiency of the mantles declines with the length of use, and that the consumption of gas per Hefner candle power, under the different conditions stated, is as follows :

Thorium oxide. Per cent.	Cerium oxide. Per cent.	Gas consumed during burning.		
		100 hours. Liters.	400 hours. Liters.	800 hours. Liters.
99.9	0.1	12	15	15
99.5	0.5	3.3	4.3	5.2
99.0	1.0	2.6	3.0	3.6
99.0	1.0	2.9	3.2	5.2

Other experiments gave :

Thorium oxide. Per cent.	Mixture.	Cerium oxide. Per cent.	Hourly consumption for one Hefner candle power.
99		1	1.7
98		2	2.2
97		3	2.4
96		4	4.2
90		10	13.0
80		20	27-34
70		30	31-85
50		50	87-110

Bunte found that pure thorium oxide gives little light (three H. C. P.), pure cerium oxide but little more (six to seven H. C. P.), while the Welsbach mixture gives about seventy H. C. P. He explains this by the theory of Drossbach, according to whom pure thorium does not react upon light waves except in presence of a small quantity of cerium, when it becomes resonant and illuminating.

Auer von Welsbach uses a filament of osmium *in vacuo* heated by the electric current, finding that it will withstand a higher temperature than carbon. It is therefore more efficient, since incandescence increases rapidly with the temperature. When heated to volatilization of platinum it gives a most agreeable white light. The osmium may contain platinum in small quantity but it must otherwise be pure. He greatly increases the luminosity by covering the osmium filament with thorium oxide.

Nernst has further developed his incandescent lamp, the value of which depends upon the power of magnesia when heated to conduct the current, to become further highly heated by the current, and in consequence of the intense heating to become incandescent. He constructs a thin cylinder of magnesia, heats it to the temperature necessary to conduction and passes the current. The light developed amounts to one Hefner unit (0.88 English unit) per watt, against one Hefner unit to three or four watts,

with the ordinary incandescent lamp. Nernst finds that even at 1000° C. magnesia does not conduct well and that its conductivity may be increased by addition of boric acid, calcium chloride, and tungstic acid. Zirconium oxide with about five per cent. of yttrium oxide; thorium oxide with twenty per cent. of yttrium oxide; thorium oxide with thirty-seven per cent. of zirconium oxide, three per cent. yttrium oxide, and three-tenths per cent. cerium oxide, likewise increase the conductivity.

The report of the Allgemeine Elektrizitäts Gesellschaft to the stockholders states that the efficiency of the light seems to be about that of a small arc-lamp; that for convenience of handling it is superior to the arc-light but inferior to the incandescent lamp. Deri mixes the earthy oxides with difficultly fusible metal or graphite, both in the form of exceedingly fine powder. The tubes or filament made with the mixture are enclosed in vacuum bulbs or are surrounded with indifferent gas. The heat developed in the conducting material is communicated to the earthy oxide, causing it to glow and become conducting.

The production of nitrogen compounds, ammonia, and cyanides, which acquired such marked impetus a few years ago, seems to have fallen into the ordinarily recognized channels, and ammonia from coal and cyanides from animal refuse still control the markets. The extension of the by-product coke ovens has increased the ammonia production and will continue to do so, and we may expect that the immediate future will offer considerably enlarged supplies. The president of the Society of Chemical Industry offers the following statistics regarding the recovery of tar and ammonia in Great Britain :

	Tar. Tons.	Ammonium sulphate. Tons.
Gas works	650,000	130,000
Shale Oil Works.....	37,000
Blast-furnaces	150,000	18,000
Recovery ovens.....	62,000	11,000
	<hr/> 862,000	<hr/> 196,000
Possible production after extension of recovery ovens.....	620,000	110,000
	<hr/> 1,482,000	<hr/> 296,000

The by-product ovens are being everywhere extended. As already stated, the number of such ovens is rapidly increasing in this country, and we may expect that the tar and ammonia production resulting therefrom will have an important influence upon the market in these commodities. In Germany, likewise, where these ovens first secured really permanent foothold, the by-products have become important factors in the nitrogen supply market.

The utilization of atmospheric nitrogen is still attractive to investigators and inventors. The fixation of free nitrogen by the soil bacteria is now fully established, and the means for stimulating this important supply of available nitrogen have become the subject of most profound study and with gratifying results.

The fixation of atmospheric nitrogen by artificial, chemical, and mechanical means has likewise been the subject of encouraging study. Lord Rayleigh's results in the removal of nitrogen from the air by its oxidation through the influence of the spark or of the silent electric discharge, has directed study to the conditions and reactions involved and the possibilities of profitable fixation of nitrogen by such means. Shenstone and Evans find that under strong electric tension atmospheric oxygen suffers contraction and ozone is formed. Eighty to eighty-three per cent. of the oxygen may be so transformed, and under certain conditions ninety-eight per cent. But if the tension acts too long, nitrogen dioxide will be formed, the ozone will suddenly be destroyed, and the oxide decomposed. Vapor of water favors the formation of nitrogen oxide which, as Rayleigh found, must quickly be removed from the electric influence to avoid decomposition.

Crookes¹ discusses his suggestion that the nitrogen supply for agricultural purposes must be obtained by artificial means from the atmosphere, and bases some calculations regarding the possibilities upon the experiments of Rayleigh in oxidizing nitrogen to obtain a residue of argon, in which, with a consumption of one horse power he obtained chemical combination of 29.4 per cent. of a nitrogen-oxygen mixture. Hence one kilowatt hour would be required for seventy-four grams of sodium nitrate and 14,000 kilowatt hours for a ton (2204 lbs.). With steam power of the highest efficiency, the cost of which is placed at 0.67 cent per kilowatt hour, the cost is stated to be \$130. With water power costing 0.15 cent per kilowatt hour the cost would become \$25. Electrolytic niter should therefore compete with the natural product, but it is questioned whether the cheap power necessary to the production of the annually required 12,000,000 tons is available.

Moissan finds that nitrogen combines with calcium at dark red heat with incandescence. At 1200° C. the product obtained is crystallized, and its composition corresponds with N_2Ca_3 . In presence of alcohol this breaks up with formation of ammonia and calcium ethylate and with cold water it yields ammonia and calcium hydroxide.

¹ Crookes says: Nitrogen is a combustible gas, and the reason why, when once ignited, the flame does not continue to spread through the atmosphere and deluge the world in a sea of nitric acid, is that the igniting-point is higher than the temperature of its flame, not high enough, therefore, to set fire to the adjacent mixture. But by passing a strong induction current between terminals the air takes fire and continues to burn with powerful flame, producing nitric and nitrous acids.

Wolfram introduces calcium carbide into a bath of fused alkali hydrate. Carbon monoxide and hydrogen are liberated, the alkali metal is set free, issues in the form of vapor, and may be collected. If nitrogen or ammonia be passed through the fused mass cyanide will be formed.

Lance and Bourgrade and Emmanuel cause a mixture of nitrogen, hydrogen, and ammonia to act upon carbon heated from 1000° to 1100° C., whereby ammonium acetylide $(\text{NH}_4)_2\text{C}_2$ is formed, and this in turn combines with nitrogen to form cyanide. Ninety per cent. of the ammonia used is converted.

Vidal proposes generation of cyanide by heating phospham to 150° – 200° C. and allowing formic acid to flow into it. Hydrocyanic acid is said to be formed and volatilized to be collected in alkali. And Vittenet heats neutral copper acetate and ammonia of 21° B. in closed tubes two hours at 180° – 185° C. White opaque scales of copper cyanide are formed.

Conroy discusses Raschen's process for production of cyanides as practiced at Widnes, near Liverpool. The process consists in treatment of sulphocyanate with nitric acid, whereby sulphur is oxidized with production of sodium sulphate, hydrocyanic acid, and nitric oxide. The volatile and gaseous products are carried along, with vapor of water, into a tower filled with stones, where the water and part of the hydrocyanic acid condenses. The greater part of the hydrocyanic acid passes over and is condensed in water while the nitric oxide is subsequently converted into nitric acid.

A most important step forward in the production of ammonia has been developed by Mond, who found that nearly 100 pounds of ammonia could be recovered per ton of fuel from producer gases by introducing along with the superheated air required to burn the fuel in the producer, two and a half tons of steam for every ton of fuel consumed. The Solvay Process Company, at Syracuse, has erected a plant of eight Mond producers at their works, replacing the use of coal in the steam plant and elsewhere. The production of fuel gas with the recovery of ammonia is said to yield a return of twenty-five per cent. profit on the capital invested.

Waisbain, working under direction of Prof. A. Lidow, undertook dry distillation of wood by passing hot deoxidized gases through the material in the retort, obtaining in a small way much better results than are obtained by the old methods. He used generator gases, controlling their temperature, and found that at 150° C. the wood is not decomposed and only hygroscopic water is removed. Between 150° and 180° C. oxygen compounds, acids, and alcohol are produced. Between 280° and 350° gaseous hydrocarbons are formed, and finally, between 350°

and 430°, tarry products are carried over. In a small way the following results were obtained :

	Birch. Per cent.	Pir. Per cent.
Hygroscopic water.....	15.0	6.00
Pyroligneous acid (21.8 per cent. acetic) ..	10.9	6.45
Methyl alcohol	1.2	1.4
Charcoal.....	31.0	31.0

In a large way, because of defective condensation, less favorable results were secured, but the yield of charcoal of good quality for metallurgical purposes was 95.5 per cent. of the theoretical.

Bach applies practically the same system in a vertical furnace consisting of three parts. In the upper part he applies superheated steam, removing hygroscopic water, and in case of pine, turpentine. In the middle part the dried wood meets an ascending current of oxygen-free gases and vapors. A lower part, corresponding with the crucible of a blast-furnace, serves for partial combustion of the resulting charcoal to furnish carbon monoxide, thus providing the deoxidized gases to be used above and the heat necessary to the distillation. In the upper part of the furnace, which is of metal, the temperature is maintained at from 150°-300° C., and methyl alcohol and some acetic acid is formed. In the lower portion of the furnace, which is of masonry, more acetic acid and tarry products are formed. The products from each portion of the furnace may be withdrawn separately.

The very striking discovery of Buchner, that extract expressed from beer yeast has the power to convert sugar directly to alcohol, has been extensively discussed and the action has been ascribed to various causes, notably the existence of living germs in the extract and the presence of living protoplasm. The possibility of spores has, however, been removed by careful filtration of the extract, and Buchner has shown that living protoplasm is not possible, first by the action of poisons, and second, by first drying the yeast and making an extract with water, which is still active. Geret and Hahn find that the extract acts likewise upon albuminoids. The action is due to an enzyme, which may be precipitated by alcohol and separated from the solution with its activity unimpaired.

Sanguinati has made a study of the application of the molds to the fermentation industries and particularly of *Aspergillus orizae* of Koji, of *Mucor alternans* (Gayon) and *Amylomyces* (Roux) from Chinese beer yeast. All these have energetic saccharifying action. *Aspergillus orizae* first, then *Amylomyces*, and finally *Mucor alternans*. In distillery practice, however, *Amylomyces* is most useful, and because of its slightly

oxidizing action, is alone effective for use in the industry. This is the form used by Collette in Lille and in other French and Belgian distilleries. He proceeds as follows: He liquefies the starch without saccharification by heating the mass with addition of a small quantity of either acid, or malt, or pure culture of the mould or the diastase therefrom, or by pulverizing the starch paste mechanically. He then boils the mass in closed vessels to complete liquefaction and sterilization, then cools and aerates with pure air and inoculates with the mould spores. Saccharification and fermentation occurs and when the operation is complete the liquid is filtered from the residues. It is claimed that an increased yield of alcohol having a fine aroma and taste has been obtained.

Emmerling made experiments to determine whether, and in what proportion, formation of glycerine and succinic acid accompanies alcoholic fermentation of sugar solutions by mold spores. To start the fermentation he used *Mucor racemosus*, easily obtained pure from horse dung. In the fermented product he found both glycerine and succinic acid, the glycerine equivalent to eight and three-tenths per cent. and succinic acid to one and four-tenths per cent. of the alcohol. The fermentation with mold spores is therefore analogous to that of yeast spores.

Simonson has concluded his interesting experiments in manufacture of alcohol from wood sawdust. The process finally adopted consisted in conversion of the carbohydrates by boiling with acid, the ratio of liquid to sawdust being at least four to one and the acid content one-half per cent. The latter was neutralized before fermentation, which was effected at 25° C., and the best result was obtained with bottom yeast. The highest yield of alcohol reached seven and seven-tenths per cent. of the air-dried wood, containing twenty per cent. of moisture and corresponded generally with sixty per cent. of that required by theory for the total sugars present in the fermented liquids. The alcohol obtained was of excellent quality.

Goldschmidt makes sodium formate by heating sodium carbonate in a current of carbon monoxide under pressure. Then he heats together four parts of the crystallized sodium formate so obtained with five parts of anhydrous sodium carbonate in glass or iron vessels with exclusion of air to 400°-410° C., obtaining a mixture of sodium oxalate and formate. This obviates the losses incurred in heating the formate alone.

Zacher proposes manufacture of oxalic acid by first drying wood sawdust *in vacuo* to 100°-150° C. to remove twenty per cent. of the moisture ordinarily present. When dry, he slowly draws in upon the mass caustic potash solution containing six to seven per cent. of carbonate, the solution becoming heated to

122° C. Then the temperature is carefully increased while the mass is being stirred until 180° C. is reached. This is maintained three hours, when the bright-yellow mass is transferred to a hot plate provided with a stirring gear. Here the temperature is brought to 320° C. and so maintained four hours. The melt is a bright gray powder which makes an almost colorless solution. It contains no unchanged cellulose, contains about thirty-two per cent. of oxalic acid, and its solution yields with lime a nearly white precipitate of calcium oxalate. The best dry sawdust is preferable and the advantageous ratio of the sawdust to the caustic is one to two.

Eitner finds that in the extraction of tannin the yield suffers severely at temperatures above 100° C. Proctor and Parker found decomposition even at 100°. Eitner gives in the following table the most favorable temperatures for extraction of the different products :

Oak bark.....	80°-90°	Myrabolum.....	90°-100°
Mimosa bark.....	70°-80°	Sumac.....	50°-60°
Fir bark.....	90°-100°	Quebracho.....	80°-90°
Valonia.....	60°-70°	Divi-divi.....	50°-60°
Trillo-valonia.....	50°-60°	Canaigre.....	40°-50°

Whether for the industry or for analysis, he recommends that extraction be effected at lower temperatures, 40°-50° C.

The retting of flax has always been a troublesome problem and the process employed from time immemorial almost has been the subject of much thought and investigation. At last a more rapid and effective process seems to have been developed by Doumer and Swarte in France. It has been the subject of a favorable report by a commission appointed by the Ministry of Agriculture in France to investigate it. The flax is subjected in closed vessels, at carefully regulated temperatures, to the action of a liquid fertilized with *Amylobacter microbes*. When the action is complete the flax is drained, washed, and, without being disturbed, dried by a current of hot air. The product is reported to be superior to that obtained by retting in the open air.

The development of the cellulose products of Cross and Bevan is being pushed vigorously, particularly in England and Germany, under the names viscose and viscid. The former is obtained by combining alkali-cellulose with carbon disulphide, forming the sulphocarbonate and making a ten per cent. solution thereof with water. Viscose so obtained may be stored and transported in vessels of wood or zinc. Iron or copper vessels are attacked by it. It may be preserved in open vessels by keeping it covered with a layer of water, but it must not be subjected to temperatures above 20° C. At 10° it will keep two weeks. It changes, by decomposition, into an elastic mass of

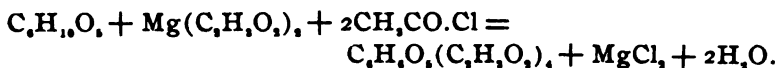
hydrocellulose but passes through stages of gelatinous or half-solid forms. For the various uses its water content and the limits of age and decomposition must be carefully determined.

All its applications depend upon the recovery of the cellulose by its spontaneous decomposition. This is hastened when the product is spread in a thin layer, and it is caused partially by the liberation of carbon disulphide, although part of the change is much more profound. The decomposition may be governed by regulation of the temperature. A film produced on glass, heated to 100° C., becomes entirely insoluble in water.

Viscose, allowed to decompose in large blocks, forms a transparent mass insoluble in water and known as *viscoid*. To insure a perfectly homogeneous product, decomposition must proceed without intervention of heat.

It has been usefully applied to the sizing of paper and tissues adding greatly to their strength. To this end the viscose, after application, must be decomposed promptly, and in the works this is effected by means of sulphur dioxide or metallic salts. The latter form insoluble sulphocarbonates, and that of zinc has been found the most effective. Goods sized with it become water-proof, and if the sizing be sufficiently thick, the finished product has the appearance of leather. It makes fine photographic films, and when spun has the appearance of silk. A wide field of usefulness is predicted for it.

The new product of the laboratories of Cross and Bevan bids fair to find many useful applications. It is cellulose tetracetate and is formed by the reaction taking place between cellulose, magnesium acetate, and acetyl chloride, as indicated in the following formula :



In manufacturing, this reaction can be carried out quantitatively. By a similar reaction the butyrate may be formed. These products are difficultly inflammable and behave with solvents like the nitrate, giving solutions of a colloidal nature. Their solubility differs from that of the nitrate. The acetate is completely insoluble in methyl alcohol, ethyl alcohol, amyl acetate, acetone, and ether, but soluble in ethyl benzoate, chloroform, epichlorhydrin, acetic anhydride, glacial acetic acid, and nitrobenzene. The solution of the tetracetate in nitrobenzene hardens, on cooling, into a solid but completely transparent jelly. The solution in chloroform, epichlorhydrin, or ethyl benzoate may be diluted to any degree with acetone without causing precipitation. Spread upon glass plates, it gives beautifully transparent films, which are continuous if their thickness is within that of iridescent films.

The tetracetate is indifferent to chemical reagents and as resistant to all acids, except nitric, as the nitrate. Aqueous alkalis, which even in the cold break up the nitrate, do not attack the tetracetate even at high temperatures. Alcoholic soda solution saponifies but does not disintegrate very thin sheets or destroy their transparency. Its insulating power is as great as that of gutta percha or rubber, and it withstands temperatures up to 150° C. In its resistance to chemical agents and its electric properties, the butyrate is similar to the acetate, but it is more soluble than the acetate and dissolves in ethyl acetate and acetone.

Weber, from whose interesting paper the facts quoted are taken, declares that these products will take the place of the nitrate in many respects, and they are particularly valuable because of their resistance to chemical agents, heat and electricity, and their non-inflammability. They are recommended for metal lac.

Fraenkel and Friedlaender find that when cotton yarn is mercerized with alcoholic alkali the strength of the product is greater than when aqueous alkali is used. Mercerization occurs only after immersion and removal from the bath. They found that yarn having a strength of 358 grams supported 553 grams after mercerization with aqueous lye of 35° B., and 618 grams when treated with cold alcoholic alkali and 720 grams with warm alcoholic lye.

Effort, directed to the production of artificial silk, continues in spite of the discouragement offered by the very low prices of the natural product. The cellulose products have thus far been the most promising and Chardonnet's process is carried on commercially. In this process cellulose is nitrated until it appears bright blue in polarized light, carefully washed and dissolved in the alcohol-ether mixture. After filtration it is spun through fine apertures, dried in chambers heated to 45° C., denitrated by alkaline sulphides, bleached, and finally, if desired, dyed with basic colors. Pauly, of Basle, dissolves carefully cleansed cotton in ammoniacal copper oxide solution, and passes the solution through fine apertures to rollers revolving in acetic acid. The fiber is washed and dried in warm air.

Stern dissolves cellulose in strong alkali and carbon disulphide, makes up to ten per cent. solution with water and forces the viscous solution through fine jets into ammonium chloride solution. It is wound on reels from this solution, washed with hot sodium carbonate solution, bleached, washed thoroughly, and dried under tension in air or a heated chamber.

Millar subjects filaments of gelatine to vapor of formaldehyde. The product is insoluble in water, takes color well, but has neither the strength nor the brilliancy of the natural product.

These are some of the advances the year has brought forth. The prevailing demand for material of every description in the arts is encouraging and must stimulate further progress, and we may reasonably believe that the near future will be fruitful in new discoveries.

WM. McMURTRIE.

NOTES.

*Chemical Detection of Vegetable Fibers.*¹—This process rests on the property which cellulose possesses of transforming itself under the action of sulphuric acid into carbohydrates, possessing an aldehydic function, which can easily be detected by the colored reaction it gives with the phenols.

The sample to be examined—suppose it to be a piece of woollen goods in which the cotton is to be detected—is, after careful washing, treated by sulphuric acid at 20° B. and heated one-half hour over the water-bath. The imperfect solution is then diluted and the carbohydrates looked for in the following way: In a test-tube about one centigram of a phenol—say resorcline—is introduced, one or two cc. of the preceding solution added, and concentrated sulphuric acid perfectly free of nitrous products poured along the side of the tube, so as not to mix it with the solution therein. The heat evolved is generally sufficient to develop a coloration at the plane of separation, and the intensity of this color can be increased if necessary by gentle heating in the water-bath. If this product resulting from the treatment of cotton is brought up to 1 part in 1000, the resorcline will give an orange, the alpha-naphthol a purple, the gallic acid a green, becoming gradually violet down in the acid, the hydroquinone and the pyrogallol a brown, the morphine and codeine a nice lavender, the thymol and menthol a pink color, etc.

The extreme sensitiveness of these reactions allows us to characterize cotton, even in dyed goods, using bone-black to decolorize the solution if absolutely necessary. An approximation as to the quantity of cellulose can be obtained by comparing the intensity of the coloration to the one given by a solution of cotton of a known strength.

As we have lately indicated, the oxycellulose, owing to its aldehydic function, gives, too, with the phenols, colored reac-

¹ Read before the Rhode Island Section, June 15, 1899.

tions and could be used to characterize the cellulose, but in the presence of wool, the formation of oxycellulose is more difficult than the transformation of cellulose into carbohydrates.

EDM. JANDRIER.

Repairing Beckmann Thermometers.—It often happens that a Beckmann thermometer is broken, leaving the inner tube, containing the mercury, intact.

I have repaired such breaks as follows:

Select a piece of glass of the same kind as is used in the thermometer (usually Jena glass) of sufficient length to take the full length of the scale, plus the length necessary to make the joint come below the scale. This is necessary in order to avoid a joint opposite the scale which would make the reading inaccurate or impossible.

Cut off the broken end at the proper point, and wrap the inner tube with a piece of asbestos three or four inches long, tying it on with a piece of wire. Slide the asbestos down until the middle of it is opposite the place where the joint is to be. Slip the large tube over the inner tube and make the joint with a small flame from a blast-lamp. Cool, and dissolve the wire from the asbestos in a suitable acid. Wash out the asbestos, and dry with alcohol and ether. Insert the scale and put on the cap.

The thermometer is practically as good as new if the joint has been properly made. Anyone who can make a *good* joint can repair a thermometer in this way.

J. C. CHRISTENSEN.

NEW BOOKS.

INDICATORS AND TEST-PAPERS: THEIR SOURCE, PREPARATION, APPLICATION AND TESTS FOR SENSITIVENESS. A *Résumé* of the Current Facts regarding the Action and Application of the Indicators and Test-papers which have been Proposed from Time to Time, and are in Present Use in Chemical Manipulations, with a Tabular Summary of the Application of Indicators. Designed for the use of Chemists, Pharmacists, and Students. BY ALFRED I. COHN, PH.G. New York: John Wiley & Sons. 1899. pp. ix + 249. Price, \$2.00.

A practically very useful compilation of the methods of preparation, uses, and tests for a very large number of indicators and

test-papers is given. The work is, unfortunately, defective in its theoretical discussions. While a very brief and not altogether satisfactory chapter is given on the theory of indicators as based on the modern theory of solutions, no use is made of the theory in other parts of the book. Statements with regard to individual indicators are almost exclusively from the purely empirical standpoint.

The theory of F. Mohr, on p. 19, can scarcely be considered otherwise than as a historical curiosity and would have been better omitted.

WILLIAM A. NOYES.

A COURSE IN QUANTITATIVE CHEMICAL ANALYSIS, GRAVIMETRIC AND VOLUMETRIC. BY NICHOLAS KNIGHT, A.M., Ph.D., New York: A. S. Barnes & Co., 1899. x + 110 pp. Price, 80 cents.

This book is offered as a course which "will constitute a sufficient basis for advanced work in organic chemistry, including the ultimate analysis of substances by combustion, and for industrial chemistry which requires quantitative methods." After a brief general introduction in regard to the care of the balance, precipitation, filtering, etc., the author devotes fifty pages to the methods of gravimetric analysis.

The choice of examples for practice is not all that can be desired. In the preliminary operations the directions given are not adequate for a beginner in analytical chemistry, neither in detail nor in substance, and do not form a sufficient foundation for the student to continue with such complex analyses as those of smaltite, tetrahedrite, and granite. The schemes for the analysis of these more complex substances would be much better suited to qualitative than to quantitative analysis, no attempts having been made to utilize the more recent and more special methods. The directions are often arbitrary and always mechanical, lacking in clearness, and with no attempt to explain the course of any reaction. Even if the student were entirely familiar with his general chemistry, he would have much trouble in trying to learn the whys and wherefores of analytical methods.

Twenty pages are devoted to volumetric analysis in the same arbitrary mechanical style. It would be useless to criticize this part of the book as well as the *seven* pages devoted to the analysis of drinking-water inasmuch as the whole of it shows a woeful lack of intimacy with the subject. The less said of the English in the book, the better; it is inexcusable.

With the many excellent treatises on analytical chemistry which can now be obtained, it is inconceivable why a new book altogether lacking in merit, should be published unless it offers new features either in contents or method.

HENRY FAY.

ERRATUM.

On page 935, October number, the symbol for rubidium persulphate should read $\text{Rb}_2\text{S}_2\text{O}_8$ or RbSO_4 .

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Essentials of Medical Chemistry, Organic and Inorganic, containing questions of Medical Physics, Chemical Philosophy, Analytical Processes, Toxicology, Etc., prepared especially for Students of Medicine. By Lawrence Wolff, M.D. Fifth Edition, Thoroughly Revised by Smith Ely Jelliffe, M.D., Ph.D. Philadelphia: W. B. Saunders. 1899. 222 pp. Price, \$1.00.

The Chemistry of Soils and Fertilizers. By Harry Snyder, Professor of Agricultural Chemistry in the University of Minnesota. Easton, Pa.: The Chemical Publishing Co. 1899. ix+277 pp. Price, \$1.50.

Practical Methods for Determining Molecular Weights. By Henry Biltz, Privatdocent at the University of Greifswald. Translated (with the Author's Sanction) by Harry C. Jones, associate in Physical Chemistry in Johns Hopkins University, and Stephen H. King, M.D., Harvard University. Easton, Pa.: The Chemical Publishing Co. 1899. ix+235 pp. Price, \$1.50.

Determination of Radicals in Carbon Compounds. By Dr. H. Meyer. Authorized translation by J. Bishop Tingle. New York: John Wiley & Sons. 1899. x+133 pp.

Preliminary Catalogue of Plants Poisonous to Stock. By V. K. Chesnut, B.S. Reprinted from the Annual Report of the Bureau of Animal Industry for 1898. 40 pp.

Experiments on the Metabolism of Matter and Energy in the Human Body. By W. O. Atwater and F. G. Benedict, with the cooperation of A. W. Smith and A. P. Bryant. U. S. Department of Agriculture, Washington, D. C. 1899. 112 pp.

Laboratory Manual. Experiments to Illustrate the Elementary Principles of Chemistry. By H. W. Hillyer, Ph.D. New York: The Macmillan Co. 1899. 200 pp. Price, 90 cents.

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WILEY, H. W. Third International Congress of Applied Chemistry (Review), 73; The Influence of Temperature on the Specific Rotation of Sucrose and Method of Correcting Readings of Compensating Polariscopes Therefor.....	568
WOODMAN, A. G. On the Determination of Added Water in Milk.....	503
WORSTALL, R. A. The Absorption of Methane and Ethane by Sulphuric Acid.....	245
XANTHINE bases in sugar-cane	609
ZINC, new method for determination of, 115; electrolytic determination in presence of manganese, 789; analysis for cadmium and lead.....	940

Proceedings.

COUNCIL.

NAME PROPOSED FOR MEMBERSHIP.

Mason, Francis Payne, 173 Broadway, Bangor, Me.

CHANGES OF ADDRESS.

Bassett, Geo. O., 30 Farnsworth St., So. Boston, Mass.
Beck, Oscar C., 383 1st St., Brooklyn, N. Y.
Cappon, Thomas W., 688 E. 139th St., N. Y. City.
Comey, Arthur M., 54 Concord Ave., Cambridge, Mass.
Eakins, L. G., care Phila. S. & R. Co., Pueblo, Colo.
Ellms, J. W., Lab. East Court & Market Sts., Cincinnati, O.
Folsom, Herbert A., Atlantic Mills, Providence, R. I.
Harding, Everhart P., Pension Villa Carola, 50 Leopold
Strasse, Heidelberg, Germany.
Miller, S. C., 18 New York Ave., N. E., Washington, D. C.
Murrill, Paul I., Hickory, N. C.
Pierce, Edw. W., 109 N. Water St., Philadelphia, Pa.
Sanders, C. N., Box 273, Bristol, Va.-Tenn.
Schedler, R. W., 405 4th St., Brooklyn, N. Y.
Schleicher, F. J., 38 W. 10th St., Long Island City, N. Y.
Seal, A. N., 405 Wister St., Germantown, Philadelphia, Pa.
Smolt, F. O., 308 W. Broadway, New York City.
Stetson, Frank O., U. S. Weather Bureau, Washington, D. C.
Taylor, S. F., Box 513, Schoharie, N. Y.
Thatcher, R. W., 2949 Potter St., Lincoln, Nebr.
Tower, O. F., Southport, Conn.
Van Dyck, E. M., Bureau Engraving & Printing, Wash-
ington, D. C.

ADDRESSES WANTED.

Lockwood, Rhodes G., 118 Beacon St., Boston, Mass.
Jessurun, David, care of Minn. Beet-Sugar Mfg. Co., St. Louis
Park, Minn.

NEW YORK SECTION.

A special meeting of the New York Section was held on Sat-
urday, May 27th, at 8.45 P.M., Dr. Wm. McMurtrie presiding.

Dr. Doremus read a notice of the Fourth International Congress of Applied Chemistry to be held in Paris in 1900.

Dr. H. W. Wiley read a paper on "The Chemistry of Nitri-
fication," illustrated by lantern slides.

The meeting was followed by refreshments under the auspices of the Chemists' Club, Dr. C. F. Chandler, its president, presiding.

M. T. BOGERT, *Secretary pro tem.*

The regular meeting of the New York Section was held on June 9th, at 8.30 P.M., in the Assembly Room of the Chemists' Club, Dr. Wm. McMurtrie presiding.

The following papers were read :

"Apparatus for Determining the Density of Cements," by Morris Loeb.

"The Determination of Sulphur in Bitumens," by S. F. and H. E. Peckham.

"Report of the Committee on Patent Legislation," by C. C. Parsons.

The election of officers of the section for the ensuing year resulted as follows :

Chairman.—C. F. McKenna.

Secretary-Treasurer.—Durand Woodman.

Executive Committee.—Wm. McMurtrie, E. G. Love, Geo. C. Stone.

Delegates to the Scientific Alliance.—E. E. Smith, Marston T. Bogert.

A unanimous vote of thanks was given to the retiring chairman for his untiring efforts and successful work.

The secretary reported that nine regular and two special meetings had been held with an average attendance of sixty-five members. Thirty-seven papers were presented and read during the season.

After the election, Dr. McKenna took the chair and made a short address expressing his appreciation of the compliment in electing him to the chair and promising to use his best efforts to maintain the high degree of interest and success achieved by his predecessor.

DURAND WOODMAN, *Secretary.*

Proceedings.

COUNCIL.

Dr. A. P. Hallock's resignation from the finance committee was accepted May 26, and Mr. J. H. Wainwright was elected in his place June 22.

The Committee on Standards for Instruments of Measure has submitted the following report :

To the President and Members of the American Chemical Society :

Your committee, to which you have assigned the duty of making a study of the means by which the American Chemical Society can hasten the adoption of uniform systems of graduation, definite limits of accuracy, and standard methods for using all forms of measuring instruments employed in chemical laboratories, beg to make the following preliminary report :

The committee was promptly organized by correspondence after its members had been notified of their appointment by the proper officer of the Society. After much discussion the committee decided to take up first the consideration of the proper form, system of graduation, limits of accuracy, manner of labelling, and methods of using glass volumetric apparatus. The committee has made a careful study of the work that has already been done in other countries on the subject, an account of which is given on pp. 527-550 of this Journal.

Your committee accordingly submits the following recommendations for your consideration :

1. That the American Chemical Society, in a manner consistent with its constitution and by-laws, ask the U. S. Office of Weights and Measures to adopt regulations for the verification of volumetric apparatus which shall be similar in purpose and scope to the regulations of the Kaiserliche Normal-Aichungs-Commission, after due consideration of the criticisms to which the latter have been subjected.

2. That the U. S. Office of Weights and Measures be asked to give special consideration to the question of a standard tem-

perature or temperatures to be adopted for the graduation of volumetric apparatus, and to obtain as far as practicable an expression of opinion from American chemists on this point.

3. That the U. S. Office of Weights and Measures be asked to submit its regulations to the American Chemical Society, or a duly appointed committee thereof, for suggestions before final adoption by that office.

4. That the International kilogram be adopted as the standard of mass.

5. That the liter as defined by the International Committee on Weights and Measures, be adopted; *viz.*, the volume of the *mass* of a kilogram of pure water at the temperature of maximum density and under a pressure of 760 mm. of mercury.

6. That all density determinations be referred to water at its maximum density and under a pressure of 760 mm. of mercury.

7. That all temperatures be expressed in terms of the hydrogen thermometer of the International Bureau of Weights and Measures.

8. That if any question arise as to the interpretation of the above definitions, the decision and standards of the U. S. Office of Standard Weights and Measures shall be accepted by the Society as final.

E. E. Ewell, *Chairman.*

Louis A. Fischer.

H. P. Talbot.

C. E. Linebarger.

G. E. Barton.

April 13, 1899.

Committee.

This report has been adopted by the Council, and the President has been authorized to make the formal requests of the U. S. Office of Weights and Measures recommended in the report.

NAMES PROPOSED FOR MEMBERSHIP.

Hand, W. F., Agricultural College, Miss.

Howell, E. Vernon, Chapel Hill, N. C.

Meaker, W. Lathrop, Longdale, Va.

NAME PROPOSED FOR ASSOCIATE MEMBERSHIP.

Butler, Robert H., 406 E. Sandusky Ave., Bellefontaine, Ohio.

NEW MEMBERS ELECTED JULY 10, 1899.

Eckfeldt, Jacob B., U. S. Mint, Philadelphia, Pa.

Ellery, James B., 12 Ellsworth Ave., Cambridge, Mass.

Gifford, Wm. E., 69 6th St., Long Island City, N. Y.
 Goldman, A., 45 Cedar St., New York City.
 Griffith, Mary D., 3914 Walnut St., Philadelphia, Pa.
 Heidenhain, Heinrich, Price Baking Powder Co., Michigan
 St. and Dearborn Ave., Chicago, Ill.
 Hough, George J., 2235 Sheridan Pl., Evanston, Ill.
 Lengfeld, Felix, University of Chicago, Chicago, Ill.
 McClement, W. T., Armour Inst., Chicago, Ill.
 Meyer, Frederick L., 2028 Park Ave., Philadelphia.
 Miller, Armand R., 812 Euclid Ave., Kansas City, Mo.
 Moore, Russell W., Appraiser's Stores, Washington and
 Christopher Sts., N. Y. City.
 Newman, Jacob W., Empire Hotel, N. Y. City.
 Perkins, Albert S., Dorchester High School, Boston, Mass.
 Plainney, John I., Cambridge Latin School, Cambridge, Mass.
 Schlichting, Emil, 61 Hicks St., Brooklyn, N. Y.
 Tower, Olin F., Adelbert College, Cleveland, O.
 Van Slyke, Lucius L., Expt. Station, Geneva, N. Y.
 Williams, Lawrence S., Armour Inst., Chicago, Ill.
 Woods, R. M., Plano Mfg. Co., West Pullman, Ill.

ASSOCIATES ELECTED JULY 10, 1899.

Allen, Lucius E., 213 E. Liberty St., Ann Arbor, Mich.
 Semonite, R. G. C., 910A Green Ave., Brooklyn, N. Y.

CHANGES OF ADDRESS.

Appleton, H. A., 42 Crossfield St., Warrington, Lancashire,
 Eng.
 Ashley, Harrison E., 947 Acushnet Ave., New Bedford, Mass.
 Boot, J. C., Director of the Experimental Station of the Klat-
 tensche Cultuur Maatschappij in Klatten, Java, Dutch East
 Indies.
 Brewer, Chas. E., 70 Huestis St., Ithaca, N. Y.
 Coburn, Arthur S., 49 Oak St., Lowell, Mass.
 Harris, Edward P., The Lakewood School, Lakewood, N. J.
 Henderson, W. E., 41 W. 11th Ave., Columbus, Ohio.
 Hewitt, Edward R., 119 E. 18th St., N. Y. City.
 James, Joseph H., Washington C. H., Ohio.
 Kelly, F. G., Henderson, N. C.
 Lindauer, A. M., 3312 Calumet Ave., Chicago, Ill.
 Liska, Anton, 1440 So. 4th Court, Chicago, Ill.
 Mooers, Chas. A., care Agr. Expt. Sta., Knoxville, Tenn.
 Nichols, H. T., Linares, S. José, N. Leon, Mexico.
 Peckham, Stephen F., 54 Downing St., Brooklyn, N. Y.
 Perry, Chas. M., 238 Cottage St., Pawtucket, R. I.
 Prentice, W. P., 52 Broadway, N. Y. City.

(72)

Schoch, Eugene P., Kent Chem. Lab., Univ. of Chicago, Chicago, Ill.

Smolt, F. O., 308 W. Broadway, Butte, Mont.

Wentworth, W. V., care Penobscot Chem. Fibre Co., Great Works, Me.

Weston, Robert Spurr, 14 Beacon St., Boston, Mass.

Proceedings.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

Benton, S. Irving, 249 E. Logan Sq., Philadelphia, Pa.
Keller, Cornelius, La Gran Fundicion Central Mexicana,
Aguas Calientes, Mexico.
Tuschka, Otto, La Gran Fundicion Central Mexicana, Aguas
Calientes, Mexico.

CHANGES OF ADDRESS.

Acker, Charles E., cor. Third St. and Walnut Ave., Niagara
Falls, N. Y.
Blair, A. W., Lake City, Fla.
Coburn, Arthur S., 49 Oak St., Lowell, Mass.
Hough, George J., Cerralbo, Nuevo Leon, Mexico.
Kilgore, B. W., Raleigh, N. C.
Mahon, R. W., 1778 Second Ave., Pittsburg, Pa.
Meyer, Gustav M., 59 E. 77th St., New York City.
Perry, Chas. M., 268 Cottage St., Pawtucket, R. I.
Sherman, H. C., Ash Grove, Virginia.

MEETINGS OF THE SECTIONS.

PHILADELPHIA SECTION.

The second meeting of this section was called to order in the Harrison Laboratory, University of Pennsylvania, at 8.15 P. M., June 8th., by the presiding officer, eleven members and visitors being present.

The minutes of the last meeting were read and approved. The secretary read a letter from the secretary of the American Chemical Society, calling attention to some changes in the list of members, and notifying us that the Philadelphia Section was entitled to one representative on the council.

The report of the By-Laws was read, accepted and adopted as a whole.

The secretary cast the ballot in the election of the following

officers : Mr. Taggart, Dr. Matthews, and Dr. Shinn as members of the Executive Committee, and Dr. John Marshall member of the council for the remainder of the current year.

The following papers were read :

"The Determination of Nickel in Nickel-Steel," by Geo. Wm. Sargent, Laboratory of the Carpenter Steel Co., Reading, Pa., read by the secretary.

A paper descriptive of a very compact apparatus for the analysis of illuminating and other gases, by Geo. E. Thomas.

"An Electrolytic Study of Benzoin and Benzil," by J. H. James, read by Dr. Hardin.

The meeting was adjourned at 9.40 P.M.

F. E. DODGE, *Secretary.*

Proceedings.

NINETEENTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY. MINUTES.

The nineteenth general meeting of the American Chemical Society was called to order at 11.30 A.M., August 21, 1899. The session was held in the chemical lecture room of Townshend Hall, at the Ohio State University, Columbus.

Minutes of the previous meeting, as recorded in the secretary's book, were approved.

The Committee on Coal Analysis made a final report through its chairman, William A. Noyes. The report was accepted and the committee discharged.

The final report of the Committee on Duty-free Importations was presented by Chas. E. Munroe, chairman. The society accepted the report and the committee was discharged.

The report of the Committee on Standards for Instruments of Measure was accepted as already printed in the Journal of the society.

A report of progress of the Committee on Patents and Related Legislation was presented by the chairman, Chas. E. Munroe, and upon motion was accepted by the society.

The Committee on Nomenclature and Spelling of the Journal had no report to present.

The secretary presented a brief, informal report, in which it was stated that the total membership of the society at present was 1,540, consisting of active members, 1,404, associates, 128, honorary members, 8.

Since the last meeting the society has lost by death the following named members: Chas. P. Worcester, Boston, Mass.; John R.

Wagner, Drifton, Pa.; C. F. Vanderford, Knoxville, Tenn.; Henry Trimble, Philadelphia, Pa.; and Thomas L. Blalock, Baltimore, Md.; also two honorary members: namely, Sir Edward Frankland, London, England, and Professor Robt. Wilhelm Eberhard Bunsen, Heidelberg, Germany.

Professor C. E. Munroe moved that the president appoint a committee to draw up a suitable memorial with reference to Sir Edward Frankland, and another committee to prepare a memorial with reference to Professor Bunsen. The motion was adopted.

After some announcements by the secretary and Professor Weber, the society adjourned to meet in Chemical Hall, at two o'clock in the afternoon.

AFTERNOON SESSION.

The society was called to order at 2.20 P.M., by President Morley. A paper on "The Relation of Physical Chemistry to Technical Chemistry," was presented by Wilder D. Bancroft, and discussed by Messrs. Hart, Wiley, Hale, Parsons, Kahlenberg, and C. B. Dudley. The next paper "On the Constitution of the Oxyazo Compounds," was presented by the author, William McPherson, and discussed by Messrs. Bancroft and McPherson. The next paper was "Upon the Nature of the Change from Violet to Green in Solutions of Chromium Salts," by W. R. Whitney. This was discussed by Messrs. Kahlenberg and Whitney. The afternoon session was then adjourned.

TUESDAY, AUGUST 22.

MORNING SESSION.

The society was called to order at 10.15 A.M., in the chemical lecture room at Townshend Hall. President Morley announced the following committees: on Frankland Memorial, Edgar F. Smith, William A. Noyes and Albert B. Prescott; on Bunsen Memorial, Albert C. Hale, W. F. Hillebrand and H. W. Wiley.

The secretary then read a paper "On the Analysis of Zinc for Cadmium and Lead," prepared by P. A. Mackay. This was followed by a paper "On the Electrolytic Deposition of Metals from Non-aqueous Solutions," by Louis Kahlenberg. This paper was discussed by Dr. Hart.

A report of progress of the Committee on Standards for Instruments of Measure, was read by the secretary in the absence of the chairman of the committee. The secretary also read a communication from Dr. C. A. Doremus, with reference to the proposed Fourth International Congress on Applied Chemistry, to be held in Paris, July 3 to 31, 1900.

After some announcements by the secretary and by Professor Weber, the society listened to an address entitled, "Some Experimental Illustrations of the Electrolytic Dissociation Theory," by Arthur A. Noyes. The address was fully illustrated by experiments.

President Morley announced that the council had decided to hold the winter meeting of the society in New Haven, Conn. He then declared the morning session adjourned.

AFTERNOON SESSION.

The first paper presented in the afternoon was upon the "Improvement in the Chemical Composition of the Corn Kernel," by C. G. Hopkins. This was discussed by Messrs. Weber, Wiley, Hale, Dudley, and Howard. The next paper was upon "Some New Products of Maize Stalks," by H. W. Wiley and W. H. Krug, read by Dr. Wiley. The secretary then read a paper on "The Chromic Acid Test for Cocaine," prepared by Geo. L. Schaefer.

Upon motion of Dr. Wiley, the thanks of the society were tendered to the Columbus Section of the American Chemical Society, the Local Committee of the American Association for the Advancement of Science, the faculty and trustees of the Ohio State University, and to Professor H. A. Weber, in particular, also to the citizens of Columbus generally, all of whom have been unsparing in their efforts to promote the interests of the nineteenth general meeting of the American Chemical Society and to give the visiting chemists a most cordial welcome and entertainment.

After a few announcements the president declared the nineteenth general meeting of the society adjourned.

ALBERT C. HALE, *Secretary*.

The Fourth International Congress of Applied Chemistry is to be held in Paris from the 23rd to the 31st of July, 1900, under

the patronage of the French Government, and the following named chemists as officers: Honorary President, M. Berthelot; President, M. H. Moissan; Secretary General, M. F. Dupont; Vice-presidents, MM. Durin, Deherain, Lindet, Gallois, Pellet.

The scope of the Congress can be judged from the titles of the sections. An American Committee on Organization has been formed consisting of

Section I. Analytical Chemistry.

W. L. Dudley, W. F. Hillebrand, J. H. Long, Elwyn Waller.

Section II. Inorganic Products.

Edward Hart, Edward W. Morley, J. D. Pennock.

Section III. Metallurgy, Mines, Explosives.

F. W. Clarke, C. B. Dudley, C. E. Munroe, H. H. Nicholson.

Section IV. Organic Products.

Thomas Evans, Wm. McMurtrie, Ira Remsen, Clifford Richardson, S. P. Sadtler.

Section V. Sugar Industry.

Edward Gudeman, W. D. Horne, G. L. Spencer, M. Swenson, Edward B. Voorhees.

Section VI. Fermentations.

C. A. Crampton, W. B. Rising, Alfred Springer.

Section VII. Agricultural Chemistry, Fertilisers, Cattle Feeding, Dairy.

G. C. Caldwell, L. L. Van Slyke, H. W. Wiley.

Section VIII. Hygiene, Medical and Pharmaceutical Chemistry.

W. O. Atwater, R. H. Chittenden, J. U. Lloyd, Wm. P. Mason, Wm. J. Schieffelin.

Section IX. Photography.

C. F. Chandler, J. H. Stebbins, Jr., E. R. Hewitt.

Section X. Electrochemistry.

Elihu Thomson, Edgar F. Smith, Charles A. Doremus, *Chairman.*

It is hoped that chemists will follow the example of these gentlemen and subscribe to the Congress. The subscription entitles the member to the printed proceedings which are voluminous.

Since British chemists will take an active part in the Congress, notably the Society of Chemical Industry, it behooves all who can, to contribute papers, as well as to otherwise advance the interests of the Congress.

The fee for membership is twenty francs, and may be forwarded to M. F. Dupont, Secretary General, 156 Boulevard de Magenta, Paris, France, or to Dr. Charles A. Doremus, 17 Lexington Avenue, New York City, who, as Chairman of the American Committee, will forward the same and also give further information when so requested.

COUNCIL.

The council of the American Chemical Society met in Room 200, of the Chittenden Hotel, Columbus, Ohio, at 7 P.M., August 21, 1899.

There were present the following named councilors: E. W. Morley, Albert C. Hale, Edward Hart, H. W. Wiley, W. A. Noyes, Chas. Baskerville, J. H. Long, N. W. Lord, C. E. Munroe, Edgar F. Smith, W. F. Hillebrand, John Marshall, G. C. Caldwell, A. A. Noyes, C. B. Dudley, and A. B. Prescott.

The following resolutions were adopted:

1. *Resolved*, That the dues for membership for the year 1900 shall be collected by the secretary, as in the current year, and he shall be allowed ten per cent. on all collections as compensation for his work.

2. *Resolved*, That monthly bills presented by the secretary for clerical help during the year 1900 shall be approved by the Finance Committee, and paid by the treasurer of the society, provided that the total sum called for by said bills shall not exceed \$600.

3. *Resolved*, That all persons whose nominations to membership shall have been received before the close of the nineteenth general meeting of the society are herewith passed upon by the council, and the secretary shall declare them elected to membership whenever all other requirements of the constitution regarding them as nominees to membership shall have been fulfilled.

4. *Resolved* That the editor's salary for the year 1900 be fixed at \$250.

5. *Resolved*, That the council recommend the appropriation of \$200 for the treasurer of the society during the year 1900.

6. *Resolved*, That the report of Dr. McKenna, as retiring treasurer, be printed in the Journal of the society.

7. *Resolved*, That the council herewith accepts the cordial invitation of the president and members of the faculty of Yale University, the director of the Sheffield Scientific School, and other professors of that institution and the Agricultural College to hold the winter meeting of the society in New Haven, Conn., during the last week in December, the exact date of said meeting to be fixed by the president and secretary of the society.

8. *Resolved*, That the resignation of Professor A. H. Sabin, as a member of the Finance Committee, be accepted, and that Dr. Wm. McMurtrie be herewith appointed to succeed Professor Sabin as member of said committee.

9. *Resolved*, That the council recommend to the Committee on Advertising that the entire business management of the advertising in the Journal during the remainder of the calendar year be intrusted to Dr. William McMurtrie, chairman of the Advertising Committee.

10. The report of the Committee on Foreign Postage was accepted and the committee discharged.

11. The report of the Committee on Life Membership Fund, announcing the permanent investment of funds sufficient to cover all life membership receipts up to date, was accepted, and the committee was discharged.

12. The report of the Committee on Exchanges was accepted, and the committee was discharged.

13. Upon motion, properly seconded and carried, the council appointed the following named persons as a standing Committee on Exchanges: Dr. H. C. Bolton, Washington, D. C., the editor and the librarian.

14. The Committee on Abstracts and Reviews presented a report of progress which was accepted.

15. The committee, appointed to consider and report upon appropriations for the library, presented a report, and after some discussion it was voted that the whole matter be referred back to said committee for further consideration and subsequent report.

16. The following motion of the acting librarian, Professor A. A. Breneman, was adopted, "Claims for non-receipt of the Journal from members, or subscribers, must be made within sixty days from the first day of the month corresponding to the missing number of the Journal."

17. Dr. Edgar F. Smith presented his resignation as member of the Committee on Papers and Publications. A motion to accept the resignation was defeated by unanimous vote.

18. The committee appointed to make recommendations regarding the reorganization and enlargement of the Committee on Papers and Publications, presented a report upon the subject, which had been referred back to said committee for further consideration.

19. After considerable discussion it was voted,

(1) That the Committee on Papers and Publications shall consist of nine members in addition to the editor, so chosen as to include representatives of each of the more important subdivisions of chemistry.

(2) That the subdivisions represented in said committee shall be the following: Inorganic Chemistry, Organic Chemistry, Analytical Chemistry, Physical Chemistry, Physiological Chemistry, Agricultural Chemistry, Industrial Chemistry, Mineralogical and Geological Chemistry, and Electrochemistry.

(3) That no specific divisions of the subject be announced in the publication of the committee.

(4) That each and every paper submitted for publication by the society shall be referred by the editor to that member of the committee, who, in his judgment, is best fitted to decide upon its merits, and he shall, jointly with the editor, decide finally in regard to its publication; provided, that in case of disagreement between the editor and said member, the paper shall be submitted to the president of the society for his decision.

(5) That we declare elected as members of the reorganized Committee on Papers and Publications the two present members of the committee, that is, Edgar F. Smith and John H. Long.¹

¹ Note. The remaining members of the Committee on Papers and Publications will be elected by the council through correspondence.

20. The following motion, presented by W. A. Noyes, was adopted. "It is hereby moved that the publication of names of nominees for membership in the Journal shall be considered as a notification from the secretary to the council, and that, two weeks after such publication, the secretary shall cast the ballot of the council for nominees in such list against whom no objection has been raised."

21. The following motion, presented by C. E. Munroe, was adopted, "Whereas, it is the custom for financial officers of societies to be bonded, it is hereby ordered that the treasurer of the American Chemical Society be requested by the directors to give a bond of \$5,000 on a surety company, which shall be renewed each year, the fee for this bond to be paid by the society."

22. Upon motion, properly seconded, and carried, it was ordered that the directors be requested to sell the invested funds of the society, other than the life membership fund, and to turn the proceeds into the treasury.

23. It was decided that the Committee on Papers and Publications be authorized to increase the October, November, and December numbers of the Journal for the current year, each to one hundred and fifty pages if found necessary.

24. Upon motion of Dr. Hart, the following suggestions made by Dr. Baskerville, were referred to a committee of three for consideration and recommendation, the committee to be appointed by the president. "I would suggest that on account of the twenty-fifth anniversary of the establishment of the society, a medal be given to that chemist who, in the opinion of the council, has made the most valuable contribution to chemical knowledge during the current year, and further that the medal be called the Priestley medal." President Morley appointed the following named persons to consider and report upon Dr. Baskerville's suggestion: Chas. E. Munroe, Albert B. Prescott, and J. W. Mallet.

ALBERT C. HALE,
Secretary.

TREASURER'S REPORT FROM DECEMBER 23, 1898, TO MAY 1, 1899.

REVENUE AND EXPENDITURES.

Dr.

To Journal (5 Nos.).....	\$1,591.88
" Secretary's office.....	647.76
" Librarian's "	93.85
" Treasurer's "	55.50
" Editor's "	47.17
" General expense.....	19.30
" Expenses of N. Y. meeting.....	9.60
" Reprinting Journal	115.50
" Authors' reprints.....	113.82
" Review of American Chemical Research.....	49.35

To Local Sections :

New York.....	\$203.84
Washington	100.00
North Eastern.....	318.33
Rhode Island	25.00
Nebraska	30.00
North Carolina	21.66
Lehigh Valley.....	10.00

\$708.83

To Commissions to secretary	587.50
" Life membership investment fund.....	1,300.00
" Renewal of library, new stacks, etc.....	446.82
" Balance in bank..... 877.68	
" Cash in treasurer's hands.. 5.00	882.68
	<hr/>
	\$6,669.56

Cr.

By Balance on hand Dec. 23, 1898.....	13.29
" Dues collected by secretary	5,875.00
" Subscriptions.....	538.27
" Advertisements through Chemical Publishing Co	108.00
" Interest on special investment.	35.00
" Life membership, Charles E. Munroe	100.00
	<hr/>
	\$6,669.56

CONDENSED REPORT OF THE OPERATIONS OF THE TREASURY
FROM JANUARY 1, 1892 TO MAY 1, 1899.

Received from Treasurer F. T. King, Jan. 1, 1892, \$	275.84
" " other sources	1892, 1,887.82
" " all "	1893, 2,662.93
" " " "	1894, 4,502.39
" " " "	1895, 5,216.02
" " " "	1896, 5,339.99
" " " "	1897, 5,976.48
" " " "	1898, 8,122.74
" " " " to May 1,	1899, 6,656.27
	<hr/>
	\$40,640.48

Disbursements as per vouchers.....	1892,	\$1,645.25
“ “ “ “	1893,	3,107.29
“ “ “ “	1894,	4,070.49
“ “ “ “	1895,	4,722.89
“ “ “ “	1896,	5,321.38
“ “ “ “	1897,	6,172.10
“ “ “ “	1898,	8,931.52
“ “ “ “ to May 1,.....	1899,	5,786.88
Balance to Treasurer A. P. Hallock		882.68
		<u>\$40,640.48</u>

ASSETS AND LIABILITIES.

DR.

To American Chemical Society.....	\$6,616.57
	<u>\$6,616.57</u>

CR.

By special investment fund.....	\$2,132.50
\$2000 City of N. Y. 3½ % gold bonds, due 1915	
“ Life membership fund	1,300.00
\$1000 N. Y. City 3½ % gold bond,	
due 1928	\$1,116.98
Deposited in Em. Ind. Savings Bank..	183.02
By Uncollected accounts (editor's office)	1,123.79
“ “ “ (secretary's office)	1,850.00
“ Cash in editor's hands.....	65.97
“ “ “ secretary's hands.....	144.31
	<u>\$6,616.57</u>

NEW YORK, May 1, 1899.

CHAS. F. MCKENNA, *Treasurer.*

Insurance on library \$5,000.

No bills remain unpaid. The library and stock of journals do not appear in above schedule because they have not yet been appraised. The securities have been examined and we certify that they are deposited in the vaults of the Mercantile Safe Deposit Company in this city.

The accounts of the treasurer since 1892 as set forth above have been examined, together with the books, vouchers, and securities and all have been found correct, E. & O. E.

ELWYN WALLER,

A. H. SABIN,

A. P. HALLOCK,

Finance Committee.

NEW YORK, May 1, 1899.

Transcribed from Vol. XIV, No. 1, p. 3.

ASSETS AND LIABILITIES. DECEMBER 31, 1891.

DR.

Cash in treasury.....	\$275.84
Accounts 1890	254.20
Dues	35.00
Personal accounts	166.31
	<hr/>
	\$731.35

CR.

Subscriptions, Journal.....	\$ 39.08
Back numbers, Journal	12.60
Dues and initiation fees.....	465.13
Personal accounts	20.17
American Chemical Society.....	194.37
	<hr/>
	\$731.35

NAMES PROPOSED FOR MEMBERSHIP.

Atkinson, Elizabeth A., 4109 Locust St., Phila., Pa.
 Bernhard, Adolph, Stone Creek, O.
 Blackshear, Charles C., Woman's College, Baltimore, Md.
 Chamberlain, Joseph S., Oberlin, O.
 Cox, John S., Lacka. I. and S. Co., Scranton, Pa.
 Fischer, Robert, 810 Franklin Ave., Columbus, O.
 Garrigues, W. E., Loomis, Wash.
 Johnson, F. C., 714 Union St., New Orleans, La.
 Oglesby, Wm. R., 212 E. Broad St., Chester, Pa.
 Sarles, Edgar H., Stelton, N. J.
 Saunders, A. P., Experimental Farm, Ottawa, Canada.
 Schoonmaker, H., 124 South Main St., Los Angeles, Cal.
 Shuttleworth, Arthur E., Guelph, York Co., Ontario, Canada.
 Worstall, Robert A., Purdue Univ., Lafayette, Ind.

CHANGES OF ADDRESS.

Asbury, S. E., Dept. of Agr., Raleigh, N. C.
 Avery, Samuel, Univ. of Idaho, Moscow, Idaho.
 Blanchard, Arthur A., Mass. Inst. Tech., Boston, Mass.
 Browne, Arthur B., Bearmouth, Mont.
 Closson, C. D., Box 552, Bisbee, Ariz.
 Davoll, David L., Jr., Peninsular Sugar Ref'g Co., Caro,
 Mich.
 Edgerly, D. W., care of Chilton Paint Co., College Point, N. Y.
 Guiterman, Franklin, Amer. Sm. and Ref. Co., Pueblo, Colo.
 Jameson, A. H., Phoenixville, Pa.
 Kelly, Wm. E., 262 Fifth ave., N. Y. City.

Keiser, E. H., Washington Univ., St. Louis, Mo.
 Lenher, Victor, Columbia Univ., N. Y. City.
 Murrill, Paul, 804 Monroe St., Ann Arbor, Mich.
 Peppel, S. V., 215 Murray St., Madison, Wis.
 Redding, C. R., Index, Snohomish Co., Wash.
 Roller, H. C., care of Dick, Ridout & Co., Cobourg, Ontario,
 Canada.
 Sherman, H. C., Columbia Univ., N. Y. City.
 Smith, H. Monmouth, Univ. of Syracuse, Syracuse, N. Y.
 Tower, O. F., Adelbert College, Cleveland, Ohio.
 Walter, Chas. A., care of McCoy Howe Co., 129 W. Georgia
 St., Indianapolis, Ind.

ADDRESSES WANTED.

Evans, Thos., formerly of Univ. of Cinn., Cincinnati, Ohio.
 Robeson, A. M., formerly of 371 W. 120th st., N. Y. City.

Proceedings.

BOARD OF DIRECTORS.

A meeting of the Board of Directors of the American Chemical Society was held at the Chemists' Club, New York, Friday, September 22, 1899. The following named directors were present : Messrs. McMurtrie, Doremus, Hallock, and Hale. Letters of regret for absence were received from President E. W. Morley and Dr. C. B. Dudley.

The meeting was called to order by the secretary at 8.10 P.M., and upon motion of Dr. Hallock, Dr. Wm. McMurtrie was chosen chairman *pro tem*.

Upon motion of Dr. Doremus it was ordered that the treasurer of the society be authorized and directed to pay, during the year 1900, the following sums as recommended by the council :

(1) To the secretary, ten per cent. as commission upon all dues collected by him during the year 1900.

(2) To the secretary, monthly bills for clerical help presented by him provided the total sum called for in such bills shall not exceed \$600 during the year 1900.

(3) To the editor, \$250 for salary.

(4) To the treasurer, \$200.

It was voted that the action of the council in the following cases be ratified and approved :

(1) That the Committee on Papers and Publications be authorized to increase the October, November, and December numbers of the Journal for the current year to 150 pages each, if found necessary.

(2) That it be recommended to the Committee on Advertising that the entire business management of the advertising in the Journal during the remainder of the calendar year be entrusted to Dr. Wm. McMurtrie, chairman of the Advertising Committee.

(3) That the treasurer of the society be requested to give a bond of \$5,000 on a surety company, which shall be renewed each year, the fee for the bond to be paid by the society.

The following preambles and resolutions were adopted :

WHEREAS, The council has requested that the directors shall sell the invested funds of the society, other than the life membership fund, and turn the proceeds into the treasury ; and

WHEREAS, After careful consideration, the directors have found that there is a considerable amount of available assets as shown by the accounts of the treasurer, therefore

Resolved, That the treasurer be directed to make every effort to realize upon these available assets before any sale of invested funds shall be considered.

The meeting then adjourned, subject to the call of the secretary.

ALBERT C. HALE, *Secretary*.

COUNCIL.

NAMES PROPOSED FOR MEMBERSHIP.

Bregowsky, Ivan M., care Crane Co., 52 Judd St., Chicago, Ill.

Carr, Louis B., Ouray, Colo.

Coit, James M., St. Paul's School, Concord, N. H.

Corse, Wm. M., 3553 Bogart Ave., Avondale, Cincinnati, Ohio.

Fogetty, Lucien, care Andrew Jorgens & Co., Spring Grove Ave., Cincinnati, Ohio.

Getz, Wm. H., 2087 Harrison Ave., Cincinnati, Ohio.

Gibson, Harriet Winfield, 77 Washington Ave., Newark, N. J.

Gore, Chas. Herbert, Ohio State Univ., Columbus, Ohio.

Hanson, Charles A., care Fleischmann & Co., Riverside, Cincinnati, Ohio.

Harrold, Ernest E., 169 King Ave., Columbus, Ohio.

Hartman, William Everett, 843 Lafayette Ave., Detroit, Mich.

Kohr, Donald A., Ohio State Univ., Columbus, Ohio.

Mudge, Charles W., 76 Brook St., Geneva, N. Y.

Peppel, Samuel V., Univ. of Wisconsin, Madison, Wis.

Sticht, G. A. H., care Tartar Chemical Co., 9th St. and Gowanus Canal, Brooklyn, N. Y.

Swan, Clifford N., Brookline, Mass.

Zimmele, H. B., 465 W. Broadway, N. Y. City.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Grayson, Wm., Jr., 702 S. University Ave., Ann Arbor, Mich.

Watson, Henry E. G., Lafayette College, Easton, Pa.

CHANGES OF ADDRESS.

- Allen, L. E., 215 E. Liberty St., Ann Arbor, Mich.
 Ashley, Harrison E., 42 Rutland Sq., Boston, Mass.
 Baxter, Gregory P., Haverford College, Haverford, Pa.
 Burt, M. C., Penna. Military College, Chester, Pa.
 Clark, Edmund, 105 Beech St., Flushing, N. Y.
 Coggeshall, G. W., 11 Prescott Hall, Cambridge, Mass.
 Ellery, James B., 322 Pine St., Steelton, Pa.
 Flynn, O. R., 6617 Drexel Ave., Chicago, Ill.
 Fosdick, E. H., Prospect Park, Cal.
 Franklin, Arthur I., 100 Canal St., Cleveland, O.
 Given, Arthur, 793 Milbury St., Worcester, Mass.
 Granja, Rafael, care Pelgram and Meyer, Paterson, N. J.
 Hayes-Campbell, J., Cave Spring, Ga.
 Labonde, Leon, Los Angeles, Cal.
 Lipman, J. G., 312 Farm St., Ithaca, N. Y.
 Merigold, B. S., 1691 Cambridge St., Cambridge, Mass.
 Pemberton, H., Jr., 1008 Clinton St., Philadelphia, Pa.
 Pickert, L. W., Amer. Sugar Ref. Co., Granite St., Boston, Mass.
 Sanders, C. N., Buena Vista, Va.
 Taylor, S. F., 3134 Boulevard, N. Y. City.
 Thatcher, Chas. J., care B. T. Babbitt, 82 Washington St.,
 N. Y. City.
 Walker, Percy H., care Brown & Walker, 36 Cole Building,
 Nashville, Tenn.
 Wilson, Edwards F., Box 291, Bristol, Tenn.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

The regular meeting of the Washington Section was held May 11, 1899. The first paper of the evening was read by F. W. Clarke, and was entitled "Experiments on the Constitution of Certain Silicates," by F. W. Clarke and George Steiger.

The paper cited some results obtained by Clarke and Schneider in 1889-92. The present work led to the following conclusions:

1. That pectolite is a metasilicate.
2. That the formula for pyrophyllite is possibly that of a basic dimetasilicate.
3. That calamine is probably a basic metasilicate which is in accord with the accepted formula.

With analcite a very interesting ammonia compound was formed, by heating with ammonium chloride. Other experiments agreed closely with those made by Friedel, and it was concluded that this mineral is a mixture of ortho- and trisilicates.

The last paper of the evening was read by Dr. H. N. Stokes, and was entitled "Indexing Organic Compounds."

Mr. Chestnut exhibited utensils used by the Indian women in the preparation of acorn meal.

WILLIAM H. KRUG, *Secretary*.

RHODE ISLAND SECTION.

The annual meeting of the Rhode Island Section of the American Chemical Society was held at the Squantum Club, June 15, 1899, with Mr. Edward D. Pearce as presiding officer.

The following officers were elected for the year 1899-1900: Edward D. Pearce, President; Walter E. Smith, Secretary and Treasurer; Charles S. Bush, member of the Executive Committee.

After dinner the presiding officer, Mr. Edward D. Pearce, read a paper on "Hydrometers." A paper on "Chemical Detection of Vegetable Fibers," received from Mr. Edm. Jandrier, was also presented.

WALTER E. SMITH, *Secretary*.

PHILADELPHIA SECTION.

The meeting was called to order at 8.20 P.M., September 22, 1899, in the Harrison Laboratory, University of Pa., the presiding officer in the chair. Fourteen members were present.

The secretary read the minutes of the last meeting; they were approved. The secretary stated that the New York Section of the American Chemical Society had invited the Philadelphia and Lehigh Valley Sections to meet with them on a date to be fixed.

Dr. Smith gave a very interesting report of the summer meeting of the society in Columbus, Ohio, at the request of Dr. John Marshall, councilor representing this section, who was detained on a previous engagement and was unable to be present.

The following papers were read: "On the Persulphates of Rubidium, Cesium, and Thallium," by Arnott R. Foster and Edgar F. Smith; read by Dr. Smith. "The Precipitation of Copper by Zinc," by John C. Shengle and Edgar F. Smith; read by Dr. Smith. "Action of Hydrochloric Acid Gas upon Sulphates, Selenates, Tellurates, and Phosphates," by Raymond W. Tunnell and Edgar F. Smith; read by Dr. Smith. The last paper was discussed by Drs. Meeker and Bradbury.

There being no further business, the meeting adjourned at 9.15 P.M.

F. E. DODGE, *Secretary*.

Proceedings.

BOARD OF DIRECTORS.

An adjourned meeting of the Directors of the American Chemical Society, was held at the Chemists' Club, 108 W. 55th St., New York City, Nov. 10, 1899. There were present Directors Doremus, Hale, Hallock, and McMurtrie. Letters of regret for absence were received from President Morley, Dr. Chandler, and Dr. Dudley.

The meeting was called to order by the secretary at 9.35 P.M. and, upon motion of Dr. Doremus, Dr. Wm. McMurtrie was chosen temporary chairman. The minutes of previous meetings, as printed in the Journal of the Society, were approved. After some statements regarding the financial condition of the Society made by the treasurer and the secretary the following resolution was unanimously adopted, having been presented by Dr. Doremus and seconded by Dr. Hale:

"Resolved, That the Treasurer of the American Chemical Society is hereby authorized, in harmony with the recommendation of the council to the directors, to negotiate a loan of twelve hundred dollars (\$1,200.00) for four months, and to sign a note for the Society, giving the two thousand dollar (\$2,000.00) bond owned by the Society as collateral."

The meeting was then adjourned.

ALBERT C. HALE, *Secretary.*

COUNCIL.

The council has approved the formation of a local section to be known as the Michigan Section with territory consisting of the State of Michigan, and with headquarters at the University of Michigan, Ann Arbor.

The Committee on Papers and Publications has been finally constituted by the council as follows:

Edward Hart, <i>Editor</i> ,	William A. Noyes,
W. F. Hillebrand.	Edgar F. Smith,
John H. Long,	H. N. Stokes,
William McMurtrie,	H. P. Talbot,
Arthur A. Noyes,	H. W. Wiley,

NAMES PROPOSED FOR MEMBERSHIP.

Adams, Walter O., 1776 Massachusetts Ave., No. Cambridge, Mass.

Ayer, Harold, Mass. Inst. Tech., Boston, Mass.

Baldwin, Charles E., 197 Auburn St., Cambridge, Mass.

Baldwin, De Forest, Kent Chem. Lab., New Haven, Conn.

Barnes, Bayard, Yale Univ., New Haven, Conn.

Beans, Hal T., Univ. of Nebr., Lincoln, Nebr.

Beck, Oscar C., 383 First St., Brooklyn, N. Y.

Boggs, Gilbert H., 603 S. 42nd St., Philadelphia.

Boltwood, Bertram B., Sheffield Scientific School, New Haven, Conn.

Boroschek, Leopold, 149 E. 56th St., New York City.

Breer, Louis B., Builders' Iron Foundry, Providence, R. I.

Button, Ok, Box 233, Trenton, Mich.

Casamajor, Walter, 372 Greene Ave., Brooklyn, N. Y.

Chase, March F., Mineral Point Zinc Co., Mineral Point, Wis.

Cluff, C. B., Lowell Textile School, Lowell, Mass.

Crofton, Alfred C., Vandervort Block, Pasadena, Cal.

Cross, Walter Martin, 12th and Troost Sts., Kansas City, Mo.

Cuadrado, Gaston A., Habana, Cuba.

Denham, Henry H., 146 N. Pearl St., Buffalo, N. Y.

Doolittle, R. E., Mich. State Dairy and Food Commission, Lansing, Mich.

Dustin, Guy K., 51 Prospect St., New Haven, Conn.

Fisher, Henry, 108 E. 70th St., N. Y. City.

Gerlach, Oscar, Mich. Cement Co., Coldwater, Mich.

Green, Erik H., 112 Newbury St., Boston, Mass.

Grosse, S. P., 180 6th Ave., Brooklyn, N. Y.

Hamilton Louis P., 3417 Hamilton St., Philadelphia.

Herger, Charles G., 11 Putnam St., Buffalo, N. Y.

Hopkins, Arthur J., Amherst, Mass.

Jackson, Florence, Wellesley College, Wellesley, Mass.

Johnson, Treat B., 141 College St., New Haven, Conn.

Knapp, Rudolf E., Parke Davis & Co., Detroit, Mich.

Kneeland, Frederick R., 239 W. 74th St., N. Y. City.

Lichtenstein, Alfred F., 134 Amity St., Brooklyn, N. Y.

Locke, James, Sheffield Chem. Lab., New Haven, Conn.
 Loew, Oscar, U. S. Dept. of Agr., Washington, D. C.
 Manteuffel, Adolf, Somerset Chem. Co., Bound Brook, N. J.
 Meyer, Gustave M., 59 E. 77th St., N. Y. City.
 Mixter, William E., Yale Univ., New Haven, Conn.
 Moore, F. J., Mass. Inst. Tech., Boston, Mass.
 Munson, L. S., Dept. of Agr., Washington, D. C.
 McFarland, B. W., 278 Canner St., New Haven, Conn.
 Newton, Elmer S., 3018 Cambridge Place, Washington, D. C.
 Norman, George N., South Works Lab., Ill. Steel Co.,
 Chicago, Ill.
 Olshausen, Bruno, Stanford Univ., Cal.
 Peet, B. W., Ypsilanti, Mich.
 Parker, C. Le Roy, Patent Office, Washington, D. C.
 Pemberton, Ralph, 1947 Locust St., Philadelphia, Pa.
 Phalen, William C., New Mexico Sch. of Mines, Socorro, N. M.
 Phelps, Isaac K., Kent Chem. Lab., New Haven, Conn.
 Platt, Elbert S., Waterford, N. Y.
 Post, Frank I., 243 E. 76th St., Chicago, Ill.
 Shilestone, Herbert M., 114 Pearl St., N. Y. City.
 Skinner, Herve J., 15 Chestnut St., Wakefield, Mass.
 Stead, John E., 11 Queen Terrace, Middlesbrough, Eng.
 Sullivan, Eugene C., 331 Packard St., Ann Arbor, Mich.
 Tucker, Charles W., 8 Grover St., Lynn, Mass.
 Voorhees, Gerald E., Berwick, Pa.
 Wachter, Leonard M., 45 James St., Green Island, N. Y.
 Webb, Mr., 1256 Massachusetts Ave., Cambridge, Mass.
 Wheeler, Henry L., Sheffield Chem. Lab., New Haven, Conn.
 Wolf, Ernst, 214 E. 82nd St., N. Y. City.
 Wright, Ralph G., 352 W. 115th St., N. Y. City.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Clark, Edwin H., 17 Hillhouse Ave., New Haven, Conn.
 Gillet, Ransom H., Pafraets Dael Club, Troy, N. Y.
 Goodenough, Robert J., 18 Seventh Ave., Brooklyn, N. Y.
 Merriman, Henry F., Summit, N. J.
 Mihalovitch, Sidney F., 829 Hutchins Ave., Avondale, Cin-
 cinnati, Ohio.
 McCrudden, Francis H., 134 Castle St., Boston, Mass.
 Rising, Herbert Robinson, 101 Wall St., New Haven, Conn.
 Sullivan, Robert Barry, 111 Grove St., New Haven, Conn.
 Swenarton, W. Hastings, 169 Union St., Montclair, N. Y.
 Victor, Carl Louis, 101 Wall St., New Haven, Conn.

NEW MEMBERS ELECTED OCTOBER 14, 1899.

Atkinson, Elizabeth A., 4109 Locust St., Philadelphia, Pa.

Bernhard, Adolph, Stone Creek, O.
Chamberlain, Joseph S., Oberlin, O.
Cox, John S., Lacka. I. & S. Co., Scranton, Pa.
Fischer, Robert, 810 Franklin Ave., Columbus, O.
Oglesby, William R., 212 E. Broad St., Chester, Pa.
Sarles, Edgar H., Steelton, N. J.
Saunders, A. P., Experimental Farm, Ottawa, Canada.

NEW MEMBERS ELECTED OCTOBER 28, 1899.

Blackshear, Charles C., Woman's College, Baltimore, Md.
Garrigues, W. E., Loomis, Wash.
Shuttleworth, Arthur E., Guelph, York Co., Ontario.

NEW MEMBERS ELECTED NOVEMBER 15, 1899.

Bregowsky, Ivan M., Care Crane Co., 52 Judd St., Chicago, Ill.
Carr, Louis B., Ouray, Colo.
Coit, James M., St. Paul's School, Concord, N. H.
Corse, William Malcolm, 3553 Bogart Ave., Avondale, Cincinnati, O.
Getz, William H., 2087 Harrison Ave., Cincinnati, O.
Gibson, Harriet W., 77 Washington Ave., Newark, N. J.
Gore, Charles H., Ohio State Univ., Columbus, O.
Hanson, Charles A., care Fleischmann & Co., Riverside, Cincinnati, O.
Harold, Ernst E., 169 King Ave., Columbus, O.
Hartman, Wm. E., 843 Lafayette Ave., Detroit, Mich.
Kohr, Donald A., Ohio State Univ., Columbus, O.
Mudge, Charles W., N. Y. State Agr. Exp. Station, Geneva, N. Y.
Peppel, Samuel V., Univ. of Wis., Madison, Wis.
Sticht, G. A. H., care Tartar Chemical Co., 9th St. and Gowanus Canal, Brooklyn, N. Y.
Swan, Clifford N., Brookline, Mass.
Zimmele, H. B., 465 West Broadway, N. Y. City.

ASSOCIATES ELECTED NOVEMBER 15, 1899.

Grayson, William, Jr., 702 S. University Ave., Ann Arbor, Mich.
Watson, Henry E. G., Lafayette College, Easton, Pa.

CHANGES OF ADDRESS.

Barrett, J. M., 908 S. 5th St., East Cedar Rapids, Iowa.
Beck, Oscar C., Box 5, High Bridge, N. J.
Busby, Fred E., Mass. Inst. Tech., Boston, Mass.
Conner, Samuel D., Expt. Station, Lafayette, Ind.
Eberman, W. S., Encampment, Wyoming.

- Ewell, E. E., 1804 S. St., N. W., Washington, D. C.
 Gallaher, Philip C., 120 W. 6th St., Leadville, Colo.
 Goodrich, Arthur L., 2103 Baronne St., New Orleans, La.
 Horsford, Roger F., 30 Farnsworth St., Boston, Mass.
 Kneeland, F. R., 56 W. 33rd St., N. Y. City.
 Lerch, Fred, Virginia, Minn.
 Linton, J. H., Birmingham, Ala.
 Liska, Anton, 1510 S. 41st Ave., Chicago, Ill.
 Lundteigen, A., Union City, Mich.
 Mackay, P. A., Mineral Point Zinc Co., Mineral Point, Wis.
 Magruder, E. W., Agricultural College, Miss.
 Miller, Armand R., 808 Euclid Ave., Kansas City, Mo.
 Miller, S. C., 1235 New York Ave., N. W., Washington, D. C.
 Millwood, J. P., 177 Spence St., Brooklyn, N. Y.
 Moody, Herbert R., 159 W. 105th St., N. Y. City.
 McCandless, John M., State Chemist, Atlanta, Ga.
 McCurdy, C. W., North Yakima, Wash.
 McDonnell, M. E., Box 236, Altoona, Pa.
 Neustadt, Geo. M. S., 234 E. 27th St., N. Y. City.
 Nichols, Herbert T., care Puertocitos Copper Co., Bisbee,
 Ariz.
 Norris, Albert P., 760 Massachusetts Ave., Cambridgeport,
 Mass.
 Parks, R. M., Water Valley, Miss.
 Payne, George F., Atlanta, Ga.
 Peckham, Stephen F., 51 Quincy St., Brooklyn, N. Y.
 Pullman, F. Cooper, 238 So. 3rd St., Philadelphia, Pa.
 Rutherford, Forest, care La Gran Fundicion Central Mexi-
 cana, Aguas Calientes, Mexico.
 Scudder, Heyward, Mass. Inst. Tech., Boston, Mass.
 Shepard, C. H., 212 E. 25th St., Los Angeles, Cal.
 Stiff, George, 439 Ditmar Ave., Borough of Queens, N. Y.
 City.
 Thomas, N. Wiley, Room 330, City Hall, Philadelphia, Pa.
 Tiffany, W. C., 21½ Spruce St., N. Y. City.
 Taggart, Walter T., 730 N. 20th St., Philadelphia, Pa.
 Tufts, J. L., General Chem. Co., Moro Phillips Works, 11th
 and Linden Sts., Camden, N. J.

ADDRESS WANTED.

Eustis, Allan C., formerly of 346 W. 58th St., N. Y. City.

MEETINGS OF THE SECTIONS.

PHILADELPHIA SECTION.

The meeting was called to order at 8.15 P.M., in the Harrison Laboratory, October 19, 1899, Chairman H. W. Jayne presiding. Twenty members were present. The minutes of the last meeting were read and approved.

The proposed joint meeting of the Lehigh, New York, and Philadelphia Sections to be held in New York City, was discussed, and it seemed to be the prevailing opinion that a date not earlier than the first of February, would be soon enough for the meeting.

Dr. J. Merritt Matthews, read a very interesting paper on "The Effect of Organic Radicals on the Color of Dye-stuffs."

Dr. G. W. Sargent gave a short note on "The Application of the Electric Spark to Carbon Determinations" and said that he hoped to have more to say upon this subject at a later date.

The meeting adjourned at 9.15 P.M.

The November meeting was called to order in the Harrison Laboratory, University of Pennsylvania, November 16, 1899, at 8.20 P.M., by the chairman, seventeen members being present.

The minutes of the last meeting were read and approved.

The chairman reported that the proposed joint meeting in New York had been postponed until later in the winter.

The next business being the election of a councilor it was moved, seconded, and carried that the nominations be made by acclamation. John Marshall was nominated, after which it was moved, seconded, and carried that nominations close. The secretary was instructed to cast the ballot for the nominee, who was declared elected member of council to represent this section for the term beginning January 1, 1900.

Robert Job presented a paper on "Some Causes of Excessive Friction in Bearing Metals," which he illustrated with numerous lantern slides, showing the defects of the metals as revealed by the microscope. The paper was discussed by Mr. Jones.

There being no further business, the meeting adjourned at 9.20 P.M.

F. E. DODGE, *Secretary.*

CINCINNATI SECTION.

The seventieth regular meeting took place in the Chemical Lecture Room of Hanna Hall, University of Cincinnati, on Saturday, October 14th, and was devoted to the presentation of the life work of the late Professor Bunsen. Twenty-one members were present, and President Simonson was in the chair.

After the transaction of regular business matters, papers were read by Mr. Stadermann, Prof. Hughes, Dr. Newman, and Mr. Weissmann respectively, on the contributions of Professor Bunsen to Physical, Inorganic, Organic, and Technical Chemistry. Dr. Springer and Prof. Norton then added some exceedingly interesting reminiscences of the personal side of this great chemist.

Mr. O. T. Joslin of the New York Section being present, upon request, gave a brief summary of the progress in the technical chemistry of animal products.

Upon motion, the meeting adjourned.

The seventy-first regular meeting was held on Wednesday, November 15th, in the Chemical Lecture Room of Hanna Hall, University of Cincinnati, twenty-two members being present, President Simonson in the chair.

Dr. Alfred Springer was reelected to represent the Cincinnati Section in the council for the year 1900.

Mr. E. Twitchell read an interesting paper on "Benzene-stearosulphonic Acid and Related Compounds" (U. S. Patent No. 628,503), which was supplemented by some analytical notes on this subject by President Simonson. Mr. B. M. Pilhashy then read a short paper on "A Comparison of Some Formaldehyde Tests."

Upon motion, the meeting adjourned.

S. WALDBOTT, *Secretary*.

NEW YORK SECTION.

The meeting was called to order by Chairman C. F. McKenna, at 8.25 P.M., October 6th, E. E. Smith, acting secretary, with fifty-nine members present. Total number in attendance was seventy-three.

The meeting opened with brief remarks by the chairman relative to the work of the section.

A paper entitled "Some Notes on the Year's Progress in Applied Chemistry" was presented by Wm. McMurtrie.

"Filters for Purifying Public Water Supplies," by Allen Hazen.

"The Mordanting and Dyeing of Silk," by Rafael Granja.

Discussion.—Dr. Bookman had found white spots on silk due to a fungus, which, however, did not grow on culture media. He had found that cells would absorb acids, contracting their outer layers. If placed in alkali, the acidity of the internal layers would gradually be reduced.

Next was presented a memorial tribute to Robert Wilhelm Eberhard Bunsen by former pupils, Dr. Doremus, Dr. Hodges, and Prof. Hale.

The chairman presented the subject of a joint meeting with the Philadelphia and Lehigh Valley Sections which had been considered by the Executive Committee. No action was taken.

Dr. Doremus asked for original contributions from members of the society to present at the Conference in Paris in August.

The meeting adjourned at 10.20.

E. E. SMITH, *Secretary pro tem.*

The regular meeting of the New York Section of the American Chemical Society was held in the Assembly Room of the Chemists' Club, 108 West 55th St., on Friday evening, November 10th. Sixty members were in attendance, Dr. C. F. McKenna, presiding. The following papers were read :

1. "Some Notes on the Year's Progress in Applied Chemistry," by Wm. McMurtrie.

2. "The Technical Analysis of Licorice Paste," by M. Trubek.

3. "On the Chemistry of Mucin," by P. A. Levene.

Dr. McMurtrie's continuation of his paper on "The Year's Progress in Applied Chemistry" was full of valuable material, and covered a wide range of subjects, among them the electrolytic production of alkali, the production of ozone on a large scale for bleaching oils and purification of water, improved shorter methods for manufacture of white lead, and a very full comparison of the efficiency of different gases and gas burners, as well as recent experimental work on the cause of light in the Welsbach mantle, and the best mixtures for the purpose.

The question of a joint meeting with the Philadelphia Section was brought up by the chair, who stated that it had been decided to postpone the proposed meeting until after the holidays.

DURAND WOODMAN, *Secretary*.

RHODE ISLAND SECTION.

The regular monthly meeting of the Rhode Island Section of the American Chemical Society was held October 19, 1899, at the Hope Club, 11 Benevolent St., Providence, R. I., with Mr. Edward D. Pearce as presiding officer.

Mr. Charles A. Catlin presented an informal address upon "Observations during a Recent Trip in Europe." His remarks were illustrated by two hundred and fifty pictures taken by himself during his travels.

The regular monthly meeting of the Rhode Island Section of the American Chemical Society was held November 16, 1899, at the Hope Club, Providence, R. I., with Mr. Edward D. Pearce as presiding officer.

After dinner, Prof. John H. Appleton, of Brown University, presented an address upon "Liquid Air." The speaker referred briefly to the history of progress in the liquefaction of gases, to the methods of preparing liquid air and to the proposed practical applications of the material.

WALTER R. SMITH, *Secretary*.

NORTH EASTERN SECTION.

The October meeting of the section was called to order at eight o'clock, on the evening of October 31st, in the Kidder Lecture Hall, of the Institute of Technology. There were about forty members present. After the reading and approval of the secretary's minutes, President Noyes introduced Professor A. H. Gill, who addressed the section on "Some Synthetic Oils." The composition and mode of manufacture of the oils were considered as well as the uses and values of the same. Dr. J. F. Norris then addressed the section on "Tellurium and the Periodic Law." In his address he called attention to the interest now centered about the determination of the atomic mass of tellurium especially in its relation to the periodic arrangement of the ele-

ments and described the various methods which have been, heretofore, employed to this end. He also described the work he has already done on tellurium, and the methods now to be employed in a further investigation of the subject.

Dr. Gill exhibited an ingenious adjustable ring devised by Rice and Buckminster, of Fitchburg, and designed to replace all the rings from one-half to five and one-half inches' diameter upon the usual ring stand.

The nominations of the Nominating Committee for officers of the section were received, and to the list several additional names were added from the floor. The election was postponed by unanimous vote until the November meeting.

W. R. WHITNEY, *Secretary*.

NORTH CAROLINA SECTION.

The summer meeting of the North Carolina Section was called to order by Dr. Baskerville, presiding officer, at 3 P.M., June 30, 1899, in the Lecture Room of the Chemical Division, University of North Carolina, Chapel Hill.

The secretary being absent, W. H. Pegram was appointed secretary *pro tem*.

The minutes of the annual meeting, February 11, 1899, were read and approved. Dr. Charles E. Munroe, ex-President American Chemical Society, was then introduced to the section.

Upon recommendation of the Membership Committee, the following were elected members of the section: S. E. Asbury, E. V. Howell, and B. W. Kilgore. The annual report of the secretary and treasurer was read and adopted.

The following papers were read and discussed:

"Analysis of Tennessee Phosphate Rock," by S. E. Asbury.

"Quantitative Electrolysis of Hydrochloric Acid," by J. M. Pickel.

"Absence of Solanin in the Tomato," by F. P. Venable and E. V. Howell.

"Secondary Heptylamine," by Thomas Clarke.

"Investigation of the Phenomena of Deliquescence and of the Capacity of Salts to Attract Water Vapor," by Charles R. Ely.

"On the Occurrence of Vanadium in Peat Ashes," by Charles Baskerville.

"On the Universal Distribution of Titanium," by Charles Baskerville.

"The Theory of Solutions," by W. H. Pegram.

"Condensation of Chloral with *o-p-m*-Nitrilanines," by Charles Baskerville.

"The Value of Malonic Esters in Synthesis," by Thomas Clarke.

"Iron and Ammonium Chlorides," by F. P. Venable and F. W. Miller.

There being no further business the section adjourned.

W. H. PEGRAM, *Secretary pro tem.*

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